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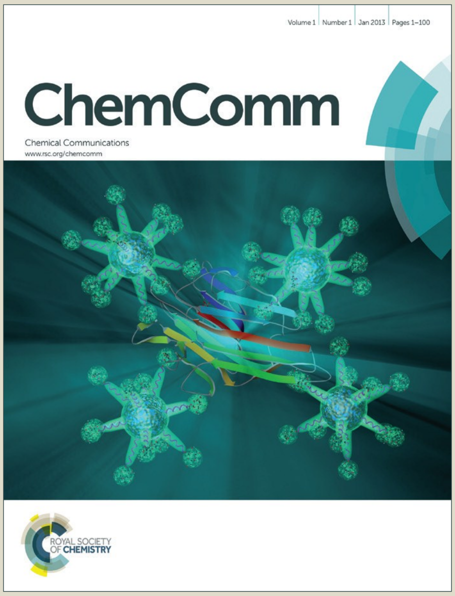

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Commercialization of Graphene-Based Technologies: A Critical Insight

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Abstract

Carbon in its single layer atomic morphology has exceptional thermal, optical, electronic and mechanical properties which may form the basis for several functional products and enhanced technologies that go from electricity storage to polymer nanocomposites of so far unsurpassed characteristics. Due to high cost, however, the current global production of graphene does not exceed 120 tonnes. New chemical and physical methods to exfoliate graphite, however, were recently engineered and commercialized, which open the route to massive adoption of graphene as the "enabler" of numerous important technologies, including enhanced electricity storage. This feature article presents an updated, critical overview that will be useful to nanochemistry and nanotechnology research practitioners and to entrepreneurs in advanced materials.

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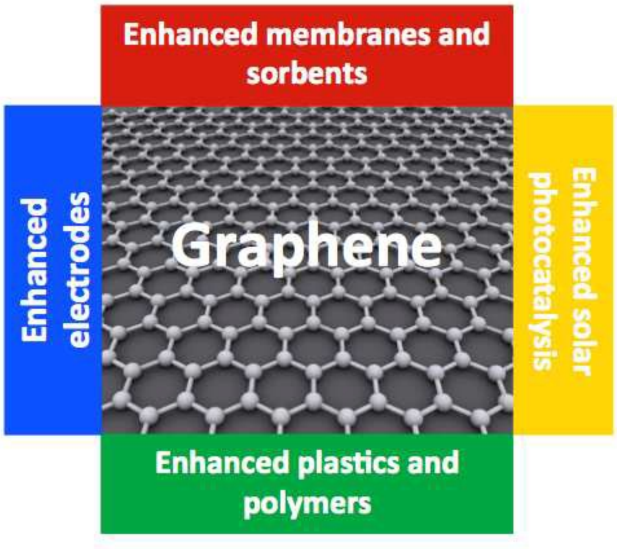

Introduction

Reminding the fullerene and carbon nanotubes (CNTs) research boom in the 1990s and early 2000s,[1] graphene has become the favorite research topic in materials chemistry and nanotechnology. Since 2004, when Geim, Novoseleov and co-workers reported the use of adhesive tape to exfoliate graphite to obtain graphene, and characterized it as a single ultrathin (0.3 nm) layer of carbon atoms arranged in two-dimension in a honeycomb lattice,[2] about 10,000 research articles have appeared in the scientific literature (Figure 1).[3]

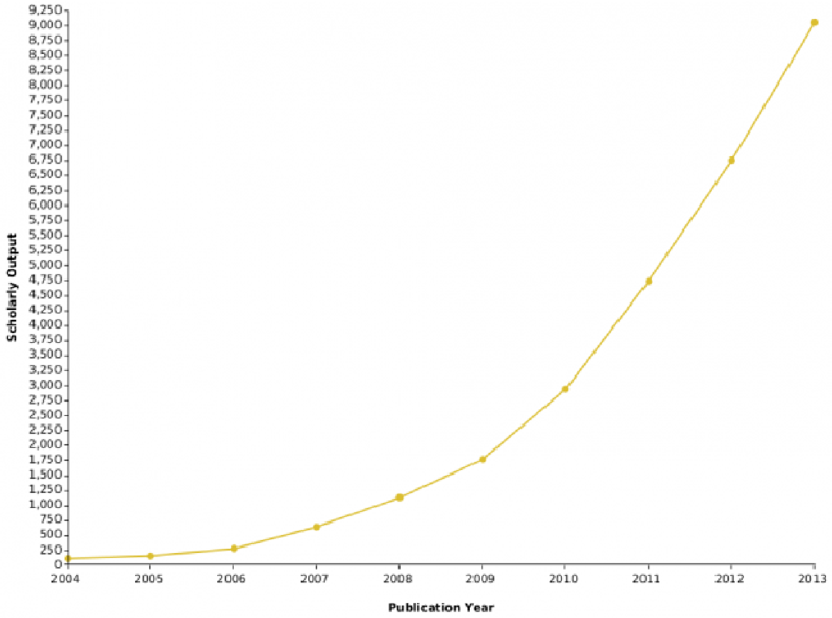

Figure 1. Scholarly output (articles only) published in the period 2004-13 from a search for "graphene" in the titles, abstracts or keywords. [Reproduced from Ref.3, with kind permission].

Graphene has 50 times the mechanical strength of steel but half the density of aluminum. Furthermore it is optically transparent and flexible. These unique properties (Table 1) derive from its unique two-dimensional atomic morphology and electronic structure,[4] and make of graphene an "enabling technology" with which to develop functional products in several areas of application.[5] Indeed, more than 10,000 patents have been granted to graphene-related technologies in just a decade,[6] since the inception of the mechanical exfoliation technique.

Table 1. Unique properties of graphene (Adapted from Ref.7, with kind permission).

Property	Reference
High electronic mobility (2.5×10^5 cm^2 V^{-1} s^{-1} at room temperature)	[8]
High thermal conductivity (>3000 WmK^{-1})	[9]
High capability to sustain high electric current densities (106 times higher than copper)	[10]
High specific surface area (2360 m^2/g of a single graphene sheet)	[11]
Extraordinary tensile elasticity (~1 TPa)	[12]
High intrinsic strength (~130 GP)	[13]
Complete impermeability to any gases	[14]
Optical transmittance (~97.7%)	[15]

Small graphene sheets and large area graphene films are already manufactured on small industrial scale in several countries (in Europe, in the US and in Asia). The market, however, is industrially not yet significant, with $ 12 million annual sales reported in 2013, and global production not exceeding 120 tonnes.[6] For comparison, production of carbon nanotubes, made of single- or multi wall graphene cylinders, in 2011 amounted to 4,000 tonnes.[16]

As commercialization of graphene-based products seems to be "within reach in a range of areas",[17] a critical insight into graphene-based technologies seems timely and useful for a balanced evaluation of the market potential of this unique material, especially considering that graphene might play a groundbreaking role in the purposeful storage, and then also in the efficient utilization of clean electricity obtained by sun and wind,[18] namely the most important technical need to solve the daily and seasonal local intermittency of solar radiation and wind availability.

A second relevant aspect is that since about 2008 chemists have started to applied different methods to synthesis of graphene materials and their derivatives by the nanochemistry bottom-up approach praised by Ozin toward different applications.[19] For example, in the context of artificial photocatalysis with graphene-semiconductor composites, chemists are learning to optimize the individual components and interfacial synergy in the composite in terms of size, shape, morphology and electronic conductivity so as to improve the electron transfer pathway, and attempt to make artificial photosynthesis of chemicals and fuels a reality.[20]

Progress in the field is so rapid that reviews covering the state of the art of graphene chemistry or nanochemistry risk to become obsolete a few months after publication. Recent progress, for example, includes the proof of concept of proton-conducting graphene membranes (though decorated with Pt nanoparticles).[21]

The aim of this work is not to provide a comprehensive review of the existing graphene nanochemistry or graphene-based technologies, but rather to articulate a critical insight into commercialization of graphene-based technologies applications written after a decade of strenuous research and entrepreneurial efforts. That such an insight might be timely is perhaps illustrated by the recent findings of Kamat and co-workers, who recently reported that reduced graphene oxide (RGO), widely proposed as a support for nanostructured catalyst particles such as TiO_2 for photocatalytic degradation of pollutants, is vulnerable toward hydroxyl radicals attack in an aqueous phase when the interfacial contact is very poor for RGO-TiO_2 composite photocatalysts.[22]

At least in Europe, no other materials science technology has received public funding of similar entity. For example, in 2013 the European Union launched a 1 billion € fund supporting research projects across Europe (the

Graphene Flagship)[23] targeting the future applications of graphene. Similarly, the United Kingdom's Government and the European Union have financed with £70 million for the creation of a National Graphene Institute in the city where the material was first isolated (Manchester).[24]

In this study, we offer a perspective view according to which we believe that numerous applications of graphene relying on the ability to transfer its exceptional properties into functional materials of enhanced characteristics will rapidly follow the recent development of low-cost graphite exfoliation chemical routes.

Enabling graphene: The new graphite exfoliation routes

In 2013, one of the world's largest chemical company exited the carbon nanotubes business as "*the potential areas of application that once seemed promising from a technical standpoint are currently either very fragmented or have few overlaps with the company's core products*".[25]

"*There is feeling*", a leading graphene industry practitioner commented at the end of 2014, "*that graphene is following in the footsteps of carbon nanotubes, which were hugely hyped in their early days too; with small incremental market share across multiple market segments*".[26]

Echoing these arguments, Banks and co-workers were asking whether or not graphene research should be attracting the large funding it is receiving, considering that carbon nanotubes did not yield many significant improvements in commercial technologies.[27] So far, indeed, CNTs have found use in new water filters, car parts, and sporting goods, which strides with huge expectations of a class of materials, widely explored since 1991 publication[28] of Iijima, originally proposed to revolutionize electronics.[29]

Yet, we argue in the following, the story of graphene-based technologies will be different, even though graphene currently continues to cost $100 to $1,000 a gram (depending on absence of defects, and crystal size and other quality parameters).[30]

Following the first decade of applied research largely financed by Governments worldwide, significant progress towards innovative graphite exfoliation methods for manufacturing high amounts of quality (defect-free) graphene layers of large surface areas has been achieved.[6]

Companies manufacturing graphene according to said rapidly evolving methods include (to mention but a few) Applied Graphene Materials, Graphoid, Incubation Alliance, Directa Plus, XG Sciences, Graphene Technologies, Graphene Frontiers, Graphenea, Haydale, Angstron, Graphensic, CVD Equipment Corporation, Graphene Supermarket and Graphene Square. In China only, the graphene industry was recently reported[31] to have an annual production capacity of small graphene sheets and large graphene films exceeding, respectively, 400 tonnes and 110,000 m^2.

To date, chemical vapor deposition of precursor gases requiring high temperature (ca. 1000 °C) and complicated transfer process, or high-temperature epitaxial growth under strictly controlled conditions, are no longer the unique methods affording graphene layers of high quality. Similarly, the multi-step solution-based method consisting in the reduction with hazardous hydrazine of graphene oxide (GO) obtained via oxidation of graphite with harsh oxidant such as $KMnO_4$ in the presence of H_2SO_4, and exfoliation of GO by sonication in a solvent is no longer the only solution-based route to achieve production of graphene micron-sized single layers (up to 20 × 40 μm in 2009).[32]

In 2014, the solution-based route based on exfoliation of graphite in liquid phase affording large platelets of pristine graphene was dramatically improved by Coleman and coworkers in Ireland, who developed a simple shear exfoliation of graphite in solution in the presence of a surfactant,[33] that goes much beyond the previously reported exfoliation route in organic solvents such as *N*-methyl-pyrrolidone whose surface energies match that of graphene.[34] It is enough to stir (with a 400 Watt blender) a suspension of graphite powder (20-50 g) in water (500 mL) containing the liquid surfactant (10-25 mL), to obtain in 10-30 minutes a large number of micrometer-sized graphene flakes suspended in water.

The first commercial shipments of graphene nanoplatelets tradenamed *Elicarb* manufactured in a pilot line affording 1 kg of product per day at chemical company Thomas Swan started in the second half of 2014.[35]

Almost concomitantly, in Canada's Ontario Grafoid opened its first production facility where high-purity *MesoGraf* graphene is produced electrochemically using a one-step chemical exfoliation process starting from unprocessed graphite ore extracted in Quebéc.[36] Developed in 2011 by Loh and co-workers at the National University of Singapore, the elegant electrolytic process uses the graphite ore as electrode. A voltage is applied to an electrolytic cell whose electrolyte includes, along with ions, intercalating organic compounds that are driven by the applied current into the interlayer spacings between the atomic interlayers of graphite, affording graphene stacked in two or three layers (multilayer graphene).

Another uniquely efficient process, developed by Mercuri,[37] starts from graphite which is thermally elongated and then exfoliated in the so called "G+" process affording a broad range of products from expanded graphite to fully exfoliated graphene nanoplatelets, each with its market value. The technology involves chemical intercalation of graphite, followed by its thermal expansion through a plasma at a temperature > 6000° C. Finally, the expanded graphite is exfoliated in liquid phase.

Since mid 2014, the technology is used by Italy's company Directa Plus to manufacture graphene sheets in a 30 tonnes per year production plant. The continuous industrial process is so efficient that the company offers a range of products at €50-500/kg (depending on the product: from super-expanded graphite to highly concentrated water-based pastes of graphene nanoplatelets).[38]

Emerging Applications

Now that low cost chemical routes to graphene have become available, applications will rapidly follow. For example, graphene-based supercapacitors are ready to be commercialized in flexible electronics like roll-up displays, TV sets, e-paper and even wearable electronics.[39]

Here we focus on three important technologies, namely cost-effective electricity storage, polymer nanocomposites and environmental remediation.

Graphene in electricity storage and utilization. Electricity is the most versatile and relevant energy form available (whether powering a cellphone or an electric vehicle, electron has become “the ultimate currency of modern industrial societies”).[40]

In today’s electricity’s “second coming-of-age”[41] scenario, batteries of lower cost, lighter and capable to recharge more rapidly are in urgent demand. Similarly, fuel cells of lower cost -- using H_2 fuel easily generated by water electrolysis[42] using today’s low cost renewable electricity -- remain to be developed and commercialized.

The development of enhanced electricity storage technologies is an urgent global need of potentially huge economic and environmental impact. Indeed, along with dramatic cost reduction, both developed and developing countries are massively adopting solar photovoltaic (PV) and wind energy to produce huge amounts of electricity. For comparison, installed solar PV capacity that reached 137 GW in 2013, was less than 1 GW in 2003.[43] In 2014 only another 45 GW were added worldwide;[44] and (in the conservative case) at least 60 GW will be installed in the course of 2015.[45]

Immense wind and solar “parks” comprising several hundreds of MW are built and connected to the grid, replacing power originating from thermoelectric power units. Notably, most of this power is installed without incentives, but rather through 20-year power purchase agreements in which a single photovoltaic kWh is sold, for example, at less than 7 c€, such as in the recent public tender of Brazil's Bahia State.[46]

Batteries, electrolyzers and fuel cells are the three main electrochemical energy technologies. All have in common the use of electrodes, many of which are comprised of graphite. Indeed, thanks to its good electrical and thermal conductivity, refractoriness and resistance to acids the hexagonal layered mineral graphite is widely used since decades to make electrodes in batteries, hydrogen fuel cells, and electrolyzers.

Graphene, with its extraordinary strength, enhanced electron conductivity (10 times more conductive than graphite), lightness, flexibility and ease of chemical processability is the ideal material with which to functionalize and enhance a conventional electrode. The use of highly conductive graphene to make both anodes and cathodes, has already led to breakthrough progress, at least on a laboratory scale;[47] even though researchers recently reviewing the field were recently first concluding that "it is not yet clear whether graphene could really lead to progress in the field";[48] to later convene that in energy storage applications "cost-effective production of graphene related materials on an industrial scale is needed to create the future energy value chain"[49].

The first major advance was reported in 2011 by Kung and co-workers who made a Li-ion battery whose anode consisting of multiple graphene sheets is able to store ten times more power (30,000 mAh instead of 3,000) with a tenfold increase in charging speed (15 minutes instead of 2 h), five times more effective after 150 charge/discharge cycles than state of the art Li-ion battery.[50] In detail, the team created tiny (10-20 nm) nanoholes in graphene sheets allowing for Li^+

ions to pass through, and introduced Si nanocrystals between each layer of graphene capable to hold four Li^+ ions.

In the complementary approach explored by Yang and co-workers, the nanostructured cathode leads to a battery capable to recharge in 20 seconds and retain more than 90 percent of its capacity even after 1000 cycles of use.[51] In detail, graphene is mixed with vanadium oxide by heating inexpensive vanadium pentoxide together with graphene oxide (GO) nanosheets in water. Single-crystalline VO_2-graphene nanoribbons for the cathode spontaneously form which serve as cathodes for ultrafast Li storage.

In Quebec the researchers of Hydro-Quebec used high-density graphene composition *MesoGraf* to form a graphene-coated lithium iron phosphate (LFP) cathode in batteries of enhanced performance in terms of power, energy density, and extended life. Multiple patents have been filed for graphene LFP batteries, addressing electric vehicle batteries and portable energy storage.[52] Already manufactured on industrial scale, batteries using lithium iron phosphate as the cathode material are capable to deliver current top values in terms of high power and energy density.

Graphene Polymer Nanocomposites. In 2008, Brinson and co-workers reported that polymer nanocomposite comprising the polymer functionalized with ultralow loadings of nanometre graphene sheets provide remarkable improvements of the thermal and mechanical properties in commodity polymers.[53] To amplify, a large shift in glass transition temperature of over 40 °C was obtained for poly(acrylonitrile) at 1 wt% graphene load; and an improvement of nearly 30 °C with only 0.05 wt% load in poly(methyl methacrylate).

Such large improvements at similar low loadings are also due to the huge interfacial area between the graphene nanofiller and polymer. Furthermore, as put by Macosko[54] graphene provides a combination of the benefits achieved with carbon nanotubes (electrical and thermal conductivity) and layered silicates (gas permeation barrier and stiffness).

Researchers at Hyundai and Kia, two car manufacturing companies, developed the use of graphene nanoparticles for stabilizing the low cost polymeric proton exchange membrane (PEM) separating the electrodes in high power density PEM fuel cells.[55] Added with a graphene nanoparticles content between 0.1 and 10 wt%, the sulfonated poly(phenylene), and poly(ether ether ketone) employed to develop inexpensive membranes, do not suffer any longer from mechanical damage due to large dimensional changes caused by water gain and loss during fuel cell operation (the ability to maintain the dynamic balance of water in the membrane-electrode in order to achieve proper membrane hydration is a critical issue affecting both performance and durability of the fuel cell; while the proton conduction ability relies on the "hopping" of protons via the -SO_3H groups in the presence of water).

Graphene, furthermore, helps to retain the flexibility, and improves the thermal resistance of the nanocomposite membrane due to higher glass transition temperature.

To understand the relevance of these findings, it should be reminded that PEMFCs are the most successful fuel cell technology with several thousand units installed worldwide.[56] Motor vehicles including automobiles, buses, trucks, boats and even aircraft[57] powered by PEMFC running on hydrogen fuel have already been built and tested for millions of km with excellent technical performance, but poor economics due to the high cost.

Such high cost stems from two components. One is the cost of Pt nanoparticles used as catalyst for the oxygen reduction reaction, the other derives from extremely expensive perfluorosulfonic acid fluorinated polymer tradenamed “Nafion” used to make the proton exchange membrane in commercial PEMFC.

At ultralow loadings, graphene nanoplatelets are able to confer excellent mechanical reinforcement. At higher concentrations, the same nanostructures provide electrical and thermal conductivity, infrared and electromagnetic shielding, and improved rheological and gas barrier properties (anti-corrosive and flame-retardancy). As economically viable graphene becomes increasingly available, the areas for applications of graphene polymer nanocomposites extend from aerospace and automotive industries to medical and consumer products of enhanced mechanical, anti-static and barrier properties, improved dimensional stability, higher resistance to micro-cracking, and extended product life.[58]

Graphene in environmental remediation. Being hydrophobic and strongly lipophilic, and with uniquely high surface area (>2300 m^2/g), graphene has exceptional capacity to adsorb organic molecules that can be exploited to purify air, soil and water contaminated with organic pollutants. Not only is 1 g of graphene obtained via plasma-exfoliated graphite able to adsorb up to 90 g of fuel oil[59] (four times higher capacity than best performing current commercial adsorbent, *Green Oil*), but graphene acts as a chemical sponge capable to rapidly adsorb and concentrate organic molecules at its surface, and remove it from the environmental matrix.

Finally, the adsorbed oils can be removed with a solvent or even by mechanical squeezing and the adsorbent recycled, saving all or most of the oil adsorbed, that will no longer be burned under controlled conditions.[60] No toxic and persistent oil dispersants, such as those used for conventional oil spill remediation, are required.

More recently, the company successfully tested the product inside a Romanian former refinery water basin containing about 16 million L of water contaminated with 56 ppm oil hydrocarbons (>1 tonne of oil to be removed; with 5 ppm being the maximum oil concentration acceptable for the discharge of treated water). Eighty kg of graphene-based product (5 g/m^3) were able to bring the hydrocarbons concentration down to 1 ppm in only 10 minutes of contact with the contaminated water. Low cost graphene has clearly enormous potential in removing different type of pollutants from contaminated water on a global scale, especially considering that pristine graphene nanoplatelets and graphene monolayer are biocompatible.[61]

Outlook and Conclusions

Five years after the isolation of graphene via physical exfoliation of graphite, trying to identify future directions in which graphene research and applications were likely to develop, Geim, a physicist, was calling attention to the fact that "*despite a cornucopia of possible findings and applications, graphene chemistry has so far attracted little interest from professional chemists*";[62] adding that "*the recent progress in making graphene suspensions has opened up a way to liquid phase chemistry, and, hopefully, the professional help that graphene researchers have long been waiting for is now coming*".[58]

Five years later, graphene has become a central topic of chemical research. Research chemists worldwide have developed the chemistry of graphene[63] and graphene oxide,[32] making new graphene-based coatings,[64] photocatalytic composites,[20] electrodes,[47-51] polymer nanocomposites,[53-57] sorbents[59-61] and selective membranes.[65] Even more importantly, chemical ingenuity resulted in the introduction of several new graphite exfoliation methods affording graphene of high crystalline quality; similar to pristine (and prohibitively costly) nanoplatelets synthesized by chemical vapor deposition.

The older multi-step process in liquid phase involving the oxidation of graphite followed by exfoliation and reduction of graphene oxide, has been supplemented by new exfoliation routes, using surfactants, electrolysis, and plasma treatment. All the latter processes have been commercialized, with the recent introduction of low cost graphene-based products priced at €50-100 per kilogram *vs* previous 100-1,000 $1000 per gram.

Graphene-based products and devices tailored to specific industrial, biomedical, electronic and optical applications will shortly emerge, amongst which we forecast cost-effective Li ion batteries, PEM fuel cells, and new sorbent materials for environmental remediation.

Many other practical applications will follow in the near future, including the chemical utilization of graphene for constructing graphene-based composites for the exploitation of visible light or sunlight in artificial photosynthesis to make chemicals and solar fuels.[20]

In conclusion, graphene will not remain a laboratory curiosity originating the publication of some 40 research papers per day.[27] This, to paraphrase Ozin[19] and Chiu,[66] will also require an educational effort through which material and chemical synthetic methods of the past are broadened and updated to "*embrace a future*" that will bring many environmental and economic benefits. Hopefully, this study will encourage such progress.

Acknowledgments

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References

1. D. Lucio-Arias, L. Leydesdorff, *Scientometrics* **2007**, *70*, 603-632.
2. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666-669.
3. A. Plume, *Research Trends*, Issue 18, September 2014. http://www.researchtrends.com/issue-38-september-2014/graphene-ten-years-of-the-gold-rush/ (last time accessed, 15 January 2015)
4. M. Koshino, T. Ando, "Electronic Properties of Monolayer and Multilayer Graphene" In *Physics of Graphene*, H. Aoki, M. S. Dresselhaus (Ed.s), Springer, New York: 2013; p. 173-208.
5. X. Zhou, W. Wang, Z. Liu, "Graphene Overview" In *Graphene: Energy Storage and Conversion Applications*, Z. Liu and X. Zhou, Ed.s, CRC Press, Boca Raton: 2014.

6. A. Zurutuza, C. Marinelli, *Nature Nanotechnol.* **2014**, *9*, 730-734.
7. L.-J. Wang, L. Li, J. Yu, Y. Wu, H. He, X. Ouyang, X. Zhao, Y.-C. Yen, L. J. Lee, *Carbon* **2014**, *79*, 294-301.
8. A. S. Mayorov, R. V. Gorbachev, S. V. Morozov, L. Britnell, R. Jalil, L. A. Ponomarenko, *Nano Lett.* **2011**, *11*, 2396-2399.
9. A. A. Balandin, *Nat. Mater.* **2011**, *10*, 569-581.
10. J. Moser, A. Barreiro, A. Bachtold, Current-induced cleaning of graphene, *Appl. Phys. Lett.* **2007**, *91*, 163513-3.
11. Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* **2010**, *22*, 3906–3924
12. C. Lee, X. Wei, W. J. Kysar, J. Hone, *Science* **2008**, *321*, 385-388.
13. F. Liu, P. M. Ming, J. Li, *Phys. Rev. B* **2007**, *76*, 064720(1)-064120(7).
14. J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead, P. L. McEuen, *Nano Lett.* **2008**, *8*, 2458-2462.
15. R. R. Nari, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, *Science* **2008**, *320*, 1308.
16. M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, A. J. Hart, *Science.* **2013**, *339*, 535-539.
17. *Nat. Nanotechnol.* **2014**, *9*, 725.
18. *Graphene: Energy Storage and Conversion Applications*, Z. Liu and X. Zhou, Ed.s, CRC Press, Boca Raton: 2014.
19. G. A. Ozin, A. Arsenault, L. Cademartiri, *Nanochemistry: A Chemical Approach to Nanomaterials,* RSC Publishing, Cambridge: 2008.
20. a) M.-Q. Yang, N. Zhang, M. Pagliaro, Y.-J. Xu, *Chem. Soc. Rev.* **2014**, *43*, 8240-8254. b) N. Zhang, Y. Zhang, Y.-J. Xu, *Nanoscale*, **2012**, *4*, 5792-5813. c) M.-Q. Yang, Y.-J. Xu, *Phys. Chem. Chem. Phys.* **2013**, *15*, 19102-19118.
21. S. Hu, M. Lozada-Hidalgo, F. C. Wang, A. Mishchenko, F. Schedin, R. R. Nair, E. W. Hill, D. W. Boukhvalov, M. I. Katsnelson, R. A. W. Dryfe, I. V. Grigorieva, H. A. Wu, A. K. Geim. *Nature* **2014**, *516*, 227-230.
22. J. G. Radich, A. L. Krenselewski, J. Zhu, P. V. Kamat, *Chem. Mater.* **2014**, *26*, 4662-4668.
23. http://graphene-flagship.eu (last time accessed, January 10, 2015).
24. http://gow.epsrc.ac.uk/NGBOViewGrant.aspx?GrantRef=EP/K005014/1 (last time accessed, January 10, 2015).
25. D. Smock, "Bayer Exits Highly Hyped Carbon Nanotubes Business", May 8, 2013. http://www.themoldingblog.com/2013/05/08/bayer-exits-highly-hyped-carbon-nanotubes-business/.
26. M. Spasenovic, "Khasha Ghaffarzadeh, Head of Consulting at IDTechEx", November 13, 2014 http://www.graphenetracker.com/khasha-ghaffarzadeh-head-consulting-idtechex/ (last time accessed, March 4, 2015).
27. E. P. Randviir, D. A.C. Brownson, C. E. Banks, *Mater. Today* **2014**, *17*, 426-432.
28. S. Iijima, *Nature* **1991**, *354*, 56-58.
29. P. Ball, *Nature* **1999**, DOI:10.1038/news991202-1
30. GE Reports, "Canada has the raw ingredient for technology's next miracle material, but will we refine it?", September 23, 2014. https://gereports.ca/canada-has-the-raw-ingredient-for-technologys-next-miracle-material-but-will-we-refine-it/ (last time accessed, January 15, 2015).
31. W. Ren, H.-M. Cheng, *Nature Nanotechnol.* **2014**, *9*, 726-730.
32. D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228-240.

33. K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S. E. O'Brien, E. K. McGuire, B. Mendoza Sanchez, G. S. Duesberg, N. McEvoy, T. J. Pennycook, C. Downing, A. Crossley, V. Nicolosi, J. N. Coleman, *Nat. Mater.* **2014**, *13*, 624-630.

34. J. N. Coleman et al., *Nat. Nanotechnol.* **2008**, *3*, 563-568.

35. http://www.thomas-swan.co.uk/news/graphene-exports-begin-uk-supplier. (last time accessed, March 4, 2015).

36. K. P. Loh, J. Wang, G. Chiu, Process for forming expanded hexagonal layered minerals and derivatives using electrochemical charging, US 20140027299 A1.

37. R. A. Mercuri, Production of Exfoliated Graphite, US Patent 20130022530.

38. Cited In: G. Cantalupo, Inaugurato il primo impianto per la produzione di grafene in Italia, *L'Industria della Gomma Elastica*, September 2014; pp. 58-62. See at the URL: http://issuu.com/edifis/docs/gomma_621_x_sfoglio/1?e=2663884/10151616 last time accessed March 4, 2015).

39. J. Zhu, D. Yang, Z. Yin, Q. Yan, H. Zhang, *Small* **2014**, *10*, 3480-3498.

40. M. Pagliaro, G. Palmisano, R. Ciriminna, *Flexible Solar Cells*, Wiley-VCH, Weinheim: 2008; p.9.

41. A. Bolduc, "Hydropower: looking to the future", 2012. http://www.hydroforthefuture.com/capsules/57/history (last time accessed March 4, 2015).

42. C. A. Rodriguez, M. A. Modestino, D. Psaltis, C. Moser. *Energy Environ. Sci.* **2014**, *7*, 3828-3835.

43. International Energy Agency, *Trends in Photovoltaic Applications*, October 2014.

44. IHS, *Q3 2014 PV Demand Market Tracker*, October 2014.

45. R. Prabhu (Mercom Capital Group), PV installations in 2015 to reach 54.5 GW, *PV Magazine*, 6 January 2015, http://www.pv-magazine.com/news/details/beitrag/pv-installations-in-2015-to-reach-545-gw_100017671/#ixzz3TKxzcJTJ (last time accessed March 4, 2015).

46. Reuters, "Enel Green Power SpA awarded 344 MW of wind and solar PV capacity in Brazilian public tender, 3 November 2014.

47. N. Mahmood, C. Zhang, H. Yin, Y. Hou, *J. Mater. Chem. A* **2014**, *2*, 15-32.

48. R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, *Nature Mater.* **2015**, *14*, 271-279.

49. F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, V. Pellegrini, *Science* **2015**, *347*, 1246501.

50. X. Zhao, C. M. Hayner, M. C. Kung, H. H. Kung, *Adv. Energy Mater.* **2011**, *1*, 1079-1084.

51. S. Yang, Y. Gong, Z. Liu, L. Zhan, D. P. Hashim, L. Ma, R. Vajtai, P. M. Ajayan, *Nano Lett.* **2013**, *13*, 1596-1601.

52. K. Zaghib et al., Lithium-ion secondary battery and method of producing same, WO 2013166598 A1.

53. T. Ramanathan, A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-Alonso, R. D. Piner, D. H. Adamson, H. C. Schniepp, X. Chen, R. S. Ruoff,, S. T. Nguyen, I. A. Aksay, R. K. Prud'Homme, L. C. Brinson, *Nat. Nanotechnol.* **2008**, *3*, 327-331.

54. H. Kim, A. A. Abdala, C. W. Macosko, *Macromolecules* **2010**, *43*, 6515-6530.

55. H. H. Lee, Hydrocarbon composite electrolyte membrane for fuel cell, US 20130065154

56. FuelCellToday, *The Fuel Cell Industry Review 2013*, Royston, UK: 2014.

57. N. Lapeña-Rey, J. Mosquera, E. Bataller, F. Ortí. *J. Aircraft* **2010**, *47*, 1825.

58. V. Mittal, *Macromol. Mater. Eng.* **2014**, *299*, 906-931.

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59. CEAR Laboratori Riuniti, Certification of oil sorbent performances of Graphene Plus, 14 October 2013, http://genius-project.com/wp-content/uploads/2014/09/131025-Oil-adsorption-certificate.pdf (last time accessed March 4, 2015).

60. A. Pola, G. Cesareo, G. Tartari, "Graphene Plus: reusable eco-innovative sorbent for oil spills clean-up and polluted water treatment", Ecomondo, Rimini, Italy, 8 November 2013. These findings are the outcome of a EU-funded project GEnIuS (Graphene Eco Innovative Sorbent, 2013-2015), following which Italy' Government approved the use of exfoliated graphite in oil spill clean-up activities.

61. J. Conroy, N. K. Verma, R. J. Smith, E. Rezvani, G. S. Duesberg, J. N. Coleman, Y. Volkov, Biocompatibility of Pristine Graphene Monolayers, Nanosheets and Thin Film, arXiv:1406.2497

62. A. K. Geim, *Science* **2009**, *324*, 1530-1534.

63. K. P. Loh, Q. Bao, P. Kailian Anga, J. Yang, *J. Mater. Chem.* **2010**, *20*, 2277-2289.

64. H. Li, Y. Huang, Y. Mao, W. L. Xu, H. J. Ploehn, M. Yu, *Chem. Commun.* **2014**, *50*, 9849-9851.

65. (a) Y. Huang, H. Li, L. Wang, Y. Qiao, C. Tang, C. Jung, Y. Yoon, S. Li, M. Yu Ultrafiltration Membranes with Structure-Optimized Graphene-Oxide Coatings for Antifouling Oil/Water Separation. *Adv. Mater. Interfaces*, DOI: 10.1002/admi.201400433; (b) H. Li, Z. Song, X. Zhang, Y. Huang, S. Li, Y. Mao, H. J. Ploehn, Y. Bao, M. Yu, *Science* **2013**, *342*, 95-98; (c) H. W. Kim, H. W. Yoon, S.-M. Yoon, B. Min Yoo, B. K. Ahn, Y. H. Cho, H. J. Shin, H. Yang, U. Paik, S. Kwon, J.-Y. Choi, H. B. Park, *Science*, **2013**, *342*, 91-95.

66. G. Chiu, "Success without borders - imagination, teamwork and graphene", TEDxSarasota, 7 November 2014.