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Mass production and industrial applications of graphene materials

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ABSTRACT

Graphene is considered a promising material for industrial application based on the intensive laboratory-scale research in the fields of physics, chemistry, materials science and engineering, and biology over the last decade. Many companies have thus started to pursue graphene materials on a scale of tons (for the flake material) or hundreds of thousands of square meters (for the film material) for industrial applications. Though the graphene industry is still in its early stages, very significant progress in mass production and certain industrial applications has become obvious. In this report, we aim to give a brief review of the mass production of graphene materials for some industrial applications and summarize some features or challenges for graphene in the marketplace.

Keywords: graphene materials, mass production, industrial application

INTRODUCTION

Graphene has attracted attention worldwide and is considered a promising material for industrial applications. Before the exfoliation of graphene with Scotch tape was reported in 2004 [1], several groups had exfoliated graphite to thin platelets [2,3], and identified 'single-layer graphite' on noble metal surfaces as grown by chemical vapor deposition (CVD) [4]. Properties and applications of graphene have been the subject of studies by the physics, chemistry, materials science, biology, biomedical and energy research communities, among others [5-7]. The 2010 Nobel Prize in Physics was awarded for "groundbreaking experiments regarding the 2D material, graphene" [1]. Around 2009, several research groups achieved breakthroughs in developing macro-scale CVD synthesis of graphene [8–10]. Earlier research on graphite oxide [6,11], its exfoliation in water and manipulation of the chemical properties of the resulting 'graphene oxide' sheets led to breakthroughs in its use in conductive polymer composites at a low loading level [12], to the generation of 'paper-like' films [13], and then later to their use as an electrode material in supercapacitors, their first use in electrical energy storage [14] and in many other applications [5, 6, 15-20]. These laboratory-scale pioneering results triggered intense interest in the mass production and industrial applications of graphene materials.

Many start-up companies as well as existing industrial enterprises have thus pursued graphene materials on a scale of tons (for the flake material from either graphite oxide or graphite itself), or hundreds of thousands of square meters (for graphene films made by CVD). They and other companies have also started to develop graphene-related products. In this report, we aim to give a brief summary of the mass production of graphene materials for some industrial applications. It is not our intent to exhaustively cover every application. We first define what is meant by graphene and 'graphene-like', briefly outline some of the basic properties of graphene and then introduce actual applications and some commercial products on the current market.

STRUCTURE AND DEFINITION OF GRAPHENE

Graphene by definition is a single layer of carbon atoms organized in a 2D, atom-thick, 'honeycomb' lattice by sp² hybridized C–C bonds between two adjacent carbon atoms (IUPAC, 1995) [21]. It is worth noting, however, that the term is used more liberally to also include materials that have

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multi-layer graphene or few-layer graphene, that is, more than one layer of graphene stacked on top of each other. Various microscopy techniques have allowed observation of the atomic lattice of suspended graphene, as well as defects such as adatoms, vacancies, holes and so on [22]. In graphene samples the atom-thick layer is mechanically compliant and so sheets (also called platelets) are often wrinkled and/or crumpled, and, in many applications, the carbon atoms in the basal plane are functionalized with various chemical groups to enable the commercial application of interest. That is, almost all 'graphene materials' are different from the idealized 2D 'graphene structure' as proposed in 1947 [23]. What is now referred to as graphene was originally obtained by surface scientists by CVD on a variety of substrates; for example, see the perspective by Ruoff [24]. Thus with reference to commercial products, it should be appreciated that 'graphene' or 'graphenelike' refers to atom-thick layers that might be chemically functionalized and contain various sorts of defects, and are used in real applications.

BASIC PROPERTIES AND APPLICATIONS PROPOSED IN LABORATORY-SCALE RESEARCH

Here we briefly summarize the basic properties and potential applications of graphene, and note that several review articles are provided here [15, 25–27].

A perfect graphene sheet is a zero-bandgap semiconductor with a cone-like band structure near the Dirac point that displays an ambipolar electric field effect in which charge carriers (electrons or holes) show a linear dispersion relationship in concentrations of up to 10^{13} cm⁻² [1,5]. In addition, graphene has a half-integer quantum Hall effect (QHE) for both electron and hole carriers and also a high electron mobility of 1.5 \times 10⁴ cm²·V⁻¹·s⁻¹ at room temperature, which is nearly independent of temperature between 10 K and 100 K [28-31]. Each additional graphene layer adds an optical absorption of ~2.3% in a broad wavelength ranging from ultraviolet to near infrared, as a consequence of graphene's electronic structure [32]. The absorption becomes saturated when the input optical intensity is above a threshold value, leading to a nonlinear optical behavior [33,34]. The thermal conductivity of suspended graphene was stated to be in the range of \sim (4.84 \pm 0.44) \times 10³ to (5.30 \pm 0.48) × 10³ W/mK at room temperature from Raman measurements [35], and it remains as high as about 600 W/mK when graphene is supported on SiO₂, exceeding the value for metals such as copper and conventional thin-film electronic materials [36]. With

a Young's modulus of 1060 GPa, and an intrinsic strength of 130 GPa, a free-standing graphene membrane has a breaking strength of 42 N/m, much stronger than steel's if one assumes a similar thickness [37,38]. Graphene is impermeable to all atoms and molecules under ambient conditions [39,40]. Hydrogen, the smallest atom, is predicted to take billions of years to penetrate graphene [41,42]. Monolayers of graphene, however, are permeable to thermal protons under ambient conditions, whereas no proton transport has been detected for bilayer graphene [43]. Although graphene is structurally stable and moderately chemically inert, chemical processing such as oxidization or fluorination may break the carbon bonding and introduce functional groups in graphene, thus bringing more variety in the properties and functions [44,45]. When functional groups are covalently attached to graphene, its highly extended pi electron cloud is disrupted, changing its electronic properties [46].

Graphene has been considered a good candidate for many applications, ranging from electronics [47,48], photonics [17,49,50], energy generation and storage [51–53], thermal management [54,58] and functional materials [12,56] to bio-applications [57,58], and many others. It is worth noting that potential applications of graphene can depend on the morphology and structure, which are mostly determined by the production methods and subsequent processing techniques. In the following, the techniques for preparing graphene, especially by mass production, are reviewed.

MASS PRODUCTION OF GRAPHENE MATERIALS

Many reviews have been published on the preparation of graphene materials on a laboratory scale [16,25,59,60], and here the focus is on the industrialscale production of graphene materials and related issues. The techniques for the mass production must be able to meet the needs for the scale of testing in industry, which is typically a kilogram of powder or suspension containing graphene flakes (typically of micrometer scale), or a thousand pieces for continuous graphene films (usually larger than millimeter size). Considering the following factors: (i) the demands of attaining the desired properties and form/morphology for target graphene products; (ii) the quality and applications of the graphene materials; (iii) the scalability from laboratory to industry; and (iv) the stability and controllability of manufacturing, we note that the current production techniques used in industry are mainly the

exfoliation of graphite, exfoliation/reduction of graphite oxide and CVD.

Direct liquid-phase exfoliation of graphite

Graphite is cheap and abundant, and the key to its exfoliation is overcoming the van der Waals interaction between graphene layers while maintaining the size of the graphene platelets. In addition to the energy input such as sonication, stirring, shearing forces, ball milling and so on, proper selection of solvents and surfactants is helpful in improving the yield of graphene platelets from graphite [61-63]. More importantly, the graphene platelets that are obtained by mechanical exfoliation potentially maintain the conjugated structure that exists in graphite, and may thus have good electrical conductivity and other properties predicted or measured for graphene. Since exfoliation is usually carried out in a solvent, its removal may cause severe restacking of the graphene platelets due to the van der Waals forces and (if present) capillary forces between them upon drying. Thus, the typical graphene products obtained from the direct exfoliation of graphite are suspensions or slurries, and the presence of solvents and other additives needs to be considered when the graphene suspensions are later used.

We have identified several companies that have reported producing graphene-containing suspensions/slurries based on the exfoliation of graphite (or similar precursors such as expanded graphite). Applied Graphene Materials plc in the UK was set up in 2010 and is advertising graphene dispersions on their website. Several companies (e.g. Ningbo MORSH, Qingdao Haoxin New Energy Technology, Dongguan SuperC Technology, Deyang Carbonene Technology) in China claim to use 'physical exfoliation' to produce graphene materials on the scale of hundreds to thousands of tons (of suspensions or slurries). For example, Dongguan SuperC Technology Ltd has announced a production capability of 10 000 tons of graphene suspension per year. As the exfoliation of graphite typically leads to a wide distribution of number of layers for the flakes, the suspensions have to be subjected to harsh separation processing to obtain graphene with a certain number of layers; chemical additives such as surfactants are often needed to keep the suspension stable for a long time. With better control of the thickness uniformity and stability, graphene materials from the direct exfoliation of graphite may have promise for use in paints and inks, as conducting additives in battery electrodes, as conducting fillers in composites and so on.

Oxidization of graphite and the subsequent exfoliation and/or reduction

Another well-known approach to exfoliate 'graphitic layers' is through oxidative intercalation using oxidizing agents such as sulfuric and nitric acids, and potassium permanganate. The oxygen functional groups in oxidized graphite are prevalent in the individual layers and thus sp³-hybridized carbon atoms are prevalent in the sp²-hybridized carbon network of the layers in graphite, leading to the product called graphite oxide [11,64–66]. Graphite oxide was first prepared by Brodie about 150 years ago [67], and was used by Boehm et al. for the preparation of thin graphene-containing platelets in 1962 [68]. With the increased interlayer distance including that due to adsorbed water, which is present as interlamellar (interlayer) H₂O molecules that are bonded both to themselves and to the epoxide and hydroxyl functional groups on the layers, a small energy input such as stirring or bath-ultrasonication could break the interaction between oxidized graphene layers and yield dispersed individual layers: 'graphene oxide'. A subsequent process to eliminate the majority of the oxygen functional groups, often called reduction but sometimes referred to as deoxygenation, can be used to partially recover the conjugated structure and electrical conductivity. Many approaches, e.g. using reducing regents to react with the oxygen functional groups, or 'burning' off the oxygen with thermal/microwave heating, irradiation, plasma/ion bombardment, have been developed to reduce graphite oxide or graphene oxide in the past decade [69–73]. Ruoff's group has demonstrated the impressive properties and potential applications of 'paper-like' materials made from graphene oxide and composites containing reduced graphene oxide mixed with polymer [12,13].

Products derived from graphite oxide include reduced graphite oxide and reduced graphene oxide powders as well as suspensions of graphene oxide made by exfoliating graphite oxide in solvents, and suspensions of reduced graphene oxide. The detailed morphology, structure and chemical components of the graphite-oxide-derived products are sensitive to the processing parameters and the equipment used, because the manufacturing processes involve chemistry and chemical engineering. This has several implications for production of 'graphene' based on graphite oxide. First, since the products are highly dependent on the manufacturing technique, products made by different companies may be very different in terms of physical morphology and chemical properties, although the companies may use similar techniques for manufacturing the graphite oxide. Second, due to the different and complicated





Figure 1. (a) Graphene production line in The Sixth Element Materials Technology Co. Ltd. (b) Graphene film production line of Wuxi Graphene Films Co. Ltd. All photos are used with permission of copyright.

morphological, structural and chemical features of graphene materials based on graphite oxide, the use (application) of such products often needs to be coordinated with the manufacturer. The complex relationship between the graphene materials and their applications may mean that most of the products from graphite oxide must be 'custom-built' and are definitely not 'one type fits all' applications. In addition, standardization for future industrial use will be difficult (but, of course, still important) because of differences in raw materials, subtle differences in manufacturing and the difficulties in its control, and the role of graphene materials in their final applications. Oxidation of graphite has been used by a few start-up companies to produce graphene materials, because the chemical processing is scalable. The Sixth Element Materials Technology (Changzhou) Co. Ltd announced a production capability of 100 tons of graphene oxide per year in 2012 (Fig. 1a). Yan Qu, CEO of The Sixth Element notes, "... we are surprised by the wide range of applications of graphite-oxide-derived materials, from thermal dissipation films, to composites, and a conducting additive in the electrode of Li-ion batteries." Further understanding of the chemistry during the materials processing of graphite oxide and of applications will be helpful in achieving products and performance with better stability and controllability.

Chemical vapor deposition (CVD)

The CVD technique used in producing industrial graphene films is mainly based on the research published in *Science* in 2009 by Ruoff's group [74], namely, the growth of graphene on Cu foil from methane and hydrogen. In 2010, Hong, who cooperated with Samsung Tech., demonstrated a prototype manufacturing line that was able to produce

rectangular graphene films 30 inches along a diagonal [75]. The CVD production of graphene typically has four steps: (i) synthesis of graphene films on metal foils such as Cu foils by CVD, (ii) removal of the metal, (iii) transfer of the graphene films onto a desired substrate, and (iv) doping the graphene film for reduced sheet resistance if needed. The CVD process can be carried out at either a low pressure (\sim 0.1 Torr) or at ambient pressure [76] and both have been applied in pilot lines for the industrial production of graphene. Currently, removing the Cu by chemical etching has been intensively used for graphene production. However, Cu accounts for more than 50% of the cost. There are several other potential methods available on a laboratory scale, e.g. electrochemical bubbling transfer [77] and electrostatic-force-assisted transfer [78], and these or other methods might be useful in the future on the industrial scale. To avoid breaking the graphene during transfer, it is protected with a covering polymer film that is removed after the graphene film has been transferred onto the target substrate. Alternatively an adhesive can be applied between the target substrate and the graphene on Cu, and the subsequent Cu etching leaves graphene on the target substrate with the adhesive layer in between. Both techniques are currently used for CVD graphene production in industry. To reduce the sheet resistance of the as-prepared CVD graphene to below 1000 ohm/sq, doping is often required, especially for the use of graphene in applications such as transparent conductors. The most popular doping agents used in industry are inorganic salts, for example, Fe(NO)3, HNO3 and AuCl, because of their processability, stability and price.

Among companies actively involved in CVD graphene production are 2D Carbon (Changzhou) Tech. Inc. Ltd, Wuxi Graphene Films Co. Ltd

and Chongqing Graphene Technology Co. Ltd in China; Graphene Square Inc. in Korea; Graphenea Inc. in Spain; BGT Materials Ltd in the UK; and Graphene Laboratories Inc. in the USA (one example is shown in Fig. 1b). Graphene Square provides graphene films with a size of up to $8 \times 8 \text{ cm}^2$ that are produced on Cu foil and then transferred onto a SiO2/Si wafer or quartz glass. Graphene films on polyethylene terephthalate (PET) with a size of $100 \times 100 \text{ cm}^2$ are available to custom order. Changzhou 2D Carbon, Wuxi Graphene Films and Chongqing Graphene Technology have announced that their annual production capacities for graphene film on Cu foil are 150 000, 100 000 and 1 000 000 m², respectively, and all are able to provide graphene films with sizes of up to 300×30 cm² on Cu foil or PET film. BGT Materials provides graphene film on SiO₂/Si or PET with sizes in the range of 1×1 to 20×25 cm². In January 2017, Graphenea announced an annual production capability of 7 000 wafers of CVD graphene with a wafer size of up to 8 inches. Graphene Laboratories are able to provide graphene on PET with sizes of <20 \times 20 cm². This information was obtained from the websites of each company.

For the further development of the CVD graphene industry, achieving (i) a wafer-scale size (or larger) of single crystal graphene and (ii) its nondestructive and clean transfer from the Cu foil (or other growth substrate if others are found) to a dielectric substrate (or other, arbitrary substrate) that satisfies the needs of industrial applications, e.g. fast processing, low price, high reliability and automatic control, are relevant. (Of course, there may be applications where polycrystalline graphene will serve sufficiently well and if it is less expensive than single-crystal material, of course it will be used.) Other challenges such as the controllable preparation of multi-layer graphene on metals and the direct growth of graphene on dielectric substrates with a quality comparable to that on Cu should also be targeted. An example is the recently reported growth of graphene on glass [79,80].

SOME COMMERCIAL APPLICATIONS OF GRAPHENE MATERIALS ON THE MARKET

Although most graphene applications are still in the demonstration stage in R&D laboratories, a few commercial applications of graphene materials have emerged onto the market. In this section, some examples in which graphene materials have demonstrated advantages over their conventional counterparts will be reviewed. We have chosen to discuss those examples that we are particularly familiar with. (As stated above, this article is not intended as an exhaustive review of all commercial applications.) It is worth noting that studies indicate that graphene holds promise for applications in electronics, optoelectronics and sensors of various types [17,20,49,81]. As the focus of this paper is on topical areas that already have products in the marketplace, we do not review these topics.

Conducting additives in electrode materials for batteries

Graphene materials have been intensely investigated as active materials or important components in electrodes for energy storage. A number of challenges need to be met before commercial products are achieved. Graphene can act as a conducting additive in electrodes to replace (at least partially) the conventionally used carbon black or carbon nanotubes. News has indicated that one of the main applications of exfoliated graphite suspensions is as a conductive additive in battery electrodes, especially for those electrode materials with an intrinsically low electric conductivity like LiFePO₄. Some of the reasons for this come from the fact that N-methyl-pyrrolidone (NMP) is a solvent suitable for both graphite exfoliation [82,83] and the electrolytes in Li-ion batteries. In addition, graphene flakes from the exfoliation of graphite usually contain less impurity and preserve most of the conjugated structure of graphene [84,62]. With higher surface areas and reasonably good electric conductivity, the amount of graphene flakes can be minimized to a value of 2 wt.% or less in the electrode, demonstrating a higher efficiency than carbon black, to achieve a similar performance of the electrode [85]. A few battery manufacturers are considering increasing the use of graphene suspensions as a conducting additive and more than hundreds of tons of graphene suspensions or slurries have been sold for this purpose. In addition, in situ introduction of graphene (or graphene oxide) materials in the procedures of fabrication of active materials may bring other advantages such as the better control of particle size of the active materials and the interface between graphene and active materials [86,87]. Given the huge development of Li-ion batteries worldwide, the market for using graphene as a conducting additive is expected to dramatically increase. One uncertainty, however, includes the choice of active materials, especially cathode materials, in batteries. Promising cathode materials, such as LiNiCoMnO₂ [88,89], have an electric conductivity much higher than LiFePO₄ so that the need for conducting additives could be further reduced or even eliminated. On the other hand,

as stated above, the difficulty in controlling the number of layers and the size distribution in exfoliated graphite could lead to problems in the stability of the additive; the effects of number of layers and flake size still need further study; and how significant the improvement in electrochemical performance of the batteries with the use of graphene additive is still under study [90]. It is worth noting that some recently developed high-capacity electrode materials, e.g. sulfur cathodes [91] or Li metal anodes [92], may provide opportunity for graphene to play other roles than purely as conducting additives.

Additives in anti-corrosion primers

Electrochemical corrosion causes considerable dam-

age and loss worldwide every year. Various coatings have been used to prevent it, among which zinc-rich epoxy is an important primer to protect less active metals such as iron. The global market for zinc-rich epoxy primers is on the scale of a few tens of millions of tons a year, leading to the consumption of a similar amount of zinc powders since the zinc content is usually more than 70 wt.% [93]. The processing of so much zinc has caused many problems in the environment and has been said to be injurious to the health of workers in related industries [94]. A few strategies, e.g. replacing some of the zinc with graphite or carbon black, have been considered in order to reduce the use of zinc in the primer. Collaborative research between The Sixth Element Materials Technology Co. (Changzhou) Inc. Ltd and the Jiangsu Toppen Technology Co. Ltd has shown that the introduction of 1 wt.% reduced graphene oxide in the primers could replace up to 50 wt.% of zinc, leading to a graphene-based zinc epoxy primer with a much lower zinc content. With the 1 wt.% graphene content (plus \sim 20 wt.% zinc), the epoxy primer has shown a nearly 4 times longer anti-corrosion life than the conventional zinc-rich epoxy primer (70 wt.% zinc) when coated on the same substrates and measured under the same conditions. Importantly, the cost of the 1 wt.% graphene powder is lower than that of the 50 wt.% of zinc that is replaced, even for the current production scale of graphene materials. The advantage of graphene in the epoxy primer is considered to be related to its effective bridging between zinc particles, resulting in an electrically conducting 3D network of zinc and graphene. During etching (corrosion), current reaches the zinc through the network of graphene platelets and the reaction of zinc protects the iron in the base. It is also perceived to be important that the distribution and stacking of graphene platelets in the epoxy physically hampers the diffusion of water or ions into the primer, thus

increasing the anti-corrosion lifetime of the primer. A demonstration of such a primer coating was carried out on a tower of a power-producing windmill in the East China Sea in December 2014, and the feedback seems satisfactory so far (Fig. 2a). Encouraged by this success, the Jiangsu Toppen Technology Co. Ltd has announced a plan to scale up the production of graphene-based zinc epoxy primers to 5000 tons per year in 2017.

A precursor for thermal dissipation films

Obviously, the current cost of graphene powder materials, compared to other bulk raw materials like steel or plastics, is still too high for them to be used as a major component in many large-scale industrial applications. This is one reason that graphene materials in the form of powders or suspensions are currently mostly used as additives. Thermal dissipation films are one area in which graphene can be used while being cost-competitive with other films, such as those from polyimide. Changzhou Fuxi Technology Co. Ltd has started to develop thermal dissipation films based on the high-temperature annealing of graphene oxide membranes (Fig. 2b). Heat treatment up to 2800 °C converts the graphene oxide membranes into high-quality 'graphite-like' membranes, but with less AB stacking due to the partial exfoliation of the graphite oxide and crumpling/folding in some of the layers in this material that is in some ways similar to graphite. The inplane thermal conductivity of such 'graphite from graphene oxide' is as high as 1500 W/mK, close to that of graphite films made from polyimide films. This high thermal conductivity has allowed heat dissipation films made from graphene oxide to be used in mobile electronics such as mobile phones or pads, with potential use in laptops and other devices in the future. In addition, graphite membranes (also referred to as films) can be produced in a thickness range from a few to hundreds of micrometers, depending on the processing of the graphene oxide membrane precursors. How the structure of the graphene platelets in the graphene oxide membranes (films) evolves during the heat treatment and affects the thermal conductivity of the as-made films is an important topic for fundamental study.

Touch panels and thermal heaters

Touch panels and thermal heaters based on CVD graphene are two functional components available for market. The Graphene Square, Changzhou 2D Carbon, Wuxi Graphene Films and Chongqing Graphene Technology can apparently produce

96 | Natl Sci Rev, 2018, Vol. 5, No. 1



Figure 2. (a) Graphene-based anti-corrosive paint applied to offshore wind turbine equipment. (b) Thermal conduction film made from graphene oxide. (c) Bracelets with double-edge curved touch sensor made of CVD graphene film. (d) Attires clothing with a heating function made of CVD graphene-based components. (e) A graphene-doped rubber tire. (f) CVD graphene films used in touch panels. All photos are used with permission of copyright.

graphene films having a size of up to meter-scale, with a sheet resistance in the range of 50-400 ohm/sq and a transmittance of > 85% on substrates, which makes the production of graphene-based touch sensors and thermal heaters possible. The excellent flexibility and chemical stability of graphene compared to its competitors, e.g. indium tin oxide (ITO) and silver nanowires, also make it an attractive conductive film for use in wearable electronics. In 2016, Wuxi Graphene Films released a bracelet with double-edge curved touch sensor made of CVD graphene film (Fig. 2c). A single-layer graphene film with a width of centimeters can conduct an electrical current of ~1 A when a voltage of 3.5 V is applied, and this can provide a heating surface with a tunable temperature of 40-120°C and thus find use in, e.g. personal-care products or clothing (Fig. 2d). The process for the production of CVD graphene-based components includes patterning of the graphene films, printing wires, and sealing with a cover, all of which require optimized processing because of the atomic-thin graphene, which is much less than that of conventional counterparts. On the other hand, the consumer electronic market, e.g. graphene touch panels, has 'cut-throat competition' and it will be of interest to see if graphene can significantly penetrate this market.

SUMMARY AND OUTLOOK

Although thousands of research papers on graphene are published every year, the graphene industry is still in its early stages. With significant progress in methods, the mass production of graphene materials has been achieved, leading to an annual production capability of hundreds to thousands of tons of graphene powder or suspensions by the chemical or physical processing of graphite, and hundreds of thousands of square meters of graphene produced by CVD on Cu. Based on the mass production (more shown in Table 1), applications of graphene materials have emerged onto the market, and some great advantages of graphene materials for certain commercial applications have become obvious. We summarize some features or challenges for graphene in the marketplace.

(i) A complete industrial chain of graphene materials is very important. As stated above, the highly preparation-sensitive structure and properties have meant that applications need very close 'communication' with production of the graphene materials. It could be helpful to the growth of industrial applications of graphene

Table 1. Some commercially available graphene products (summarized based on the information provided on their websites).

Company	Products and specifications
Applied Graphene Materials plc, UK	Dispersions: Graphene, stable, free of graphite and other metal contaminants
(http://www.appliedgraphenematerials.com,	/)
	Nanoplatelets: Graphene through bottom-up process without starting with graphite or using any oxidation procedures
Ningbo MORSH, China (http://www.nbmorsh.com/h-index.html)	Paste: Graphene in water, solid content 4.0%, pH 6–7, layer size 5–15 μ m, thickness 2.4 nm
	Powder: Graphene, apparent density 0.13 g/cm ³ , specific surface area (SSA) 5 m ² /g, layer size 5–15 μ m, thickness 2.4 nm, ash \leq 0.2%
Dongguan SuperC Technology, China	Paste: Graphene, in custom-built solvents or water, high electronic and thermal conductivity, high purity
(http://www.superc.com.cn/en/index.aspx)	
Qingdao Haoxin New Energy Technology Co. Ltd, China	Slurries: Graphene in NMP or water, solid content 4.0%, dispersant content 1%, pH 6–8, viscosity 1000–2000 mPa
(http://www.hxnano.com/english/index.asp	
	Powder : Graphene, carbon content \geq 95%, ash \leq 1%, SSA 300–800 m ² /g, 80% less than 10 layers, sheet size D ₅₀ \leq 10 μ m
Deyang Carbonene Technology, China (http://www.carbonene.cn/)	Powder: Graphene from intercalation–expansion–exfoliation; layer number 5–6, size 6–10, thickness < 3.0 nm, SS. $40-60$ m $^2/g$, ash content $(1100^{\circ}C) < 3.0\%$
The Sixth Element Materials	Powder : reduced graphite oxide (r-GO), pH 7.0–8.0, tap density < 0.1 g/cm ³ , SSA, Brunauer-Emmett-Teller
Technology (Changzhou) Co.	(BET) $\geq 120 \text{ m}^2/\text{g}$, H ₂ O content < 1.0%, particle size D ₅₀ $\leq 10.0 \mu\text{m}$, content: C > 98.0%, O < 1.0%, S < 0.1%,
Ltd, China (http://www.c6th.com/)	electrical conductivity >4000 S/m, metal ions <100 ppm
	Powder : GO, pH 1.8, tap density $<$ 1.0 g/cm ³ , C content 47 \pm 5%, SO ₄ ²⁻ content $<$ 8.0%, metal ions $<$ 100 ppm
	Wet cake: GO, solid content $45 \pm 5\%$, pH ≥ 1.2 , viscosity (GO 2 wt. % in H ₂ O) > 2000 mPa·s, SO_4^{2-} content $< 8.0\%$, metal ions < 100 ppm
	$\textbf{Paste} : \text{r-GO in NMP or H}_2\text{O, solid content 5.0\%, particle size } D_{50} \leq 6.0~\mu\text{m, viscosity 1000-3000 mPa·s, pH 7-8,}$
	impurity content ≤500 ppm
XG Sciences Inc., US	Nanoplatelets: particle diameter $<2 \mu m$, SSA 300, 500, 750 m ² /g; Particle diameter 5, 15, 25 μm , SSA 60–80 m ² /g
(http://www.xgsciences.com/products/)	Particle diameter 5, 15, 25 μ m, SSA 120–150 m ² /g
	Dispersions : in aqueous, isopropanol alcohol (IPA), organic solvents; flat particles $(5-10 \text{ nm} \text{ in thickness})$ with quite large diameters
2D Carbon	Films: Graphene on copper foil, purity 99.95%, thickness 50 μ m; Graphene on quartz glass, silicon wafer or PET
Graphene Material Co. Ltd, China (http://www.cz2dcarbon.com/en/)	substrate
	Films: Graphene heating film, efficiency of electricity to heat conversion > 80%
Wuxi Graphene Films Co. Ltd,	Films: Graphene transparent conducting film, monolayer transmittances > 88% (with PET substrate), double-layer
China (http://www.graphenefilm.com.cn/)	transmittance $>$ 86% (with PET substrate), haze $<$ 0.5%, monolayer graphene sheet resistance 220 ± 40 ohm/sq, double-layer graphene sheet resistance 150 ± 40 ohm/sq; Graphene on copper foil, monolayer graphene coverage $>$ 90%
	$\textbf{Films} : \textbf{Graphene heating film, operating voltage} < 12~\textbf{V}, \textbf{temperature uniformity} \pm 15\%, \textbf{maximum temperature}$
	120°C, resistance change < 3% after 10k times bending at bending angle of 180° and curve radius of 10 mm
	Devices: Graphene touch sensors, multi-point touch screen, transmittances >86%, haze < 1.0% Devices: Multi-touch module, multi-touch support, the surface hardness of tempered glass ≥7 H
Chongqing Graphene Technology Co. Ltd, China	Films: Graphene on copper foil, monolayer graphene coverage >99%;
(http://www.cqmxi.com/)	
	Graphene on PET, square resistance 150–200 ohm, transparency (incl. substrate) >88%;
	$Graphene \ on \ PI, square \ resistance \ 100-180 \ ohm, transparency \ (incl. \ substrate) > 83\%;$
	$Graphene\ on\ quartz\ glass,\ square\ resistance\ 150-200\ ohm,\ transparency\ (incl.\ substrate)>92\%;$
	Graphene on Si or Si/SiO ₂ wafer, square resistance 150–250 ohm, monolayer graphene coverage >96%
	Terminal devices : E-book, Graphene touch panel, 9.7', Android 4.0, resolution 1200×825 px;

Cell phone, Graphene touch panel, 5.5', Android 5.1, 1080 \times 1920 FHD; Flexible phone, Graphene touch panel, 5.1', Android 5.1, ultra-thin 6 mm

98 | *Natl Sci Rev*, 2018, Vol. 5, No. 1

Table 1. Continued.

Company	Products and specifications
Graphene Square Inc., Korea	Films: Graphene on Cu foil, size up to $500 \times 600 \text{ mm}^2$; Graphene on SiO_2/Si wafer, size up to $140 \times 140 \text{ mm}^2$;
(http://www.graphenesquare.com/)	Graphene on PET, size up to $500 \times 600 \text{ mm}^2$; Graphene on quartz glass, size up to $140 \times 140 \text{ mm}^2$: continuous monolayer >95%, sheet resistance: <250–400 ohm/sq (after transfer), mobility >3500 cm ² /Vs, transmittance >97%, domain size: \sim 10 μ m
	$\textbf{Dispersion:}~GO~(Hummers'\ method)~in~H_2O, concentration~0.1~g/100~mL, flake~size~<1~\mu\text{m},~1-atom~layer~>60\%$
Graphenea Inc., Spain	$\textbf{Films}: Graphene film, transparency > 97\%, monolayer coverage > 95\%, thickness (theoretical) 0.345 \ nm, FET (theoretical)$
(https://www.graphenea.com/)	electron mobility on Al ₂ O ₃ : 2800 cm ² /Vs, Hall electron mobility on SiO ₂ /Si: 2000–3500 cm ² /V, sheet resistance on SiO ₂ /Si: 450 \pm 40 ohm/sq, grain size up to 10 μ m, Raman spectroscopy I(G)/I(2D) < 0.5, I(D)/I(G) < 0.05; Substrate customizable
	Dispersion: GO in water, 4 mg/mL, monolayer content (measured in 0.5 mg/mL) $> 95\%$, pH 2.2–2.5, particle size D ₅₀ :14.3–16.6, EA of GO: C 49–56%, H 0–1%, N 0–1%, S 0–2%, O 41–50%
	Powder : r-GO, humidity (Karl Fischer, TGA) 3.7 – 4.2 %, electrical conductivity (at 20 nm film thickness) 6667 S/m, SSA, BET 422.69 – 499.85 m ² /g, density: 1.91 g/cm ³ , particle size (0.1 mg/mL, NMP) 260 – 290 nm, EA: C 77 – 87 % H 0 – 1 %, N 0 – 1 %, S 0 %, O 13 – 22 %
BGT Materials Ltd, U.K.	Films: Graphene on Cu foil, monolayer percentage > 95%, transmittance (at 550 nm, excl. substrate) > 97%, Ramar
(http://www.bgtmaterials.com/)	$I(D)/I(G) < 5\%$ within domain, Hall mobility of 2000–4000 cm ² /Vs at $n = 1 \times 10^{12}$ /cm ² , sheet resistance 300–600 ohm/sq;
	Graphene on SiO ₂ /Si wafer, Graphene film coverage $>$ 95% with occasional holes and cracks ($<$ 5%), monolayer percentage $>$ 95%, Raman Id/Ig $<$ 5% within domain, Hall mobility of 2000–4000 cm ² /Vs at $n = 1e12$ /cm ² , sheet resistance 300–600 ohm/sq;
	Graphene on PET, transmittance (at 550 nm, excl. substrate) $>$ 85%, sheet resistance $<$ 800 ohm/sq Dispersion : GO in DI water, 0.1–5.0 mg/mL, flake size 1–20 μ m, pH 6–7
	Devices: Graphene FET, ambipolar transport, uncovered monolayer graphene channel, field-effect carrier mobility > 2000 cm ² /Vs
Changzhou Fuxi Technology Co.	Film: Thermal conducting film, thickness 17–40 μ m, thermal conductivity 1000–1500 W/m·K, thermal diffusivity
Ltd, China.	$600-850\text{mm}2/\text{s}, \text{ density } 1.85-2.05\text{g/cm}3, \text{ specific heat capacity } 0.85\text{J/g}\cdot\text{K}, \text{ tensile strength} > 20\text{MPa}, \text{ bending } 1.85-2.05\text{g/cm}3, \text{ specific heat capacity } 0.85\text{J/g}\cdot\text{K}, \text{ tensile strength} > 20\text{MPa}, \text{ bending } 1.85-2.05\text{g/cm}3, \text{ specific heat capacity } 0.85\text{J/g}\cdot\text{K}, \text{ tensile strength} > 20\text{MPa}, \text{ bending } 1.85-2.05\text{g/cm}3, \text{ specific heat capacity } 0.85\text{J/g}\cdot\text{K}, \text{ tensile strength} > 20\text{MPa}, \text{ bending } 1.85-2.05\text{g/cm}3, \text{ specific heat capacity } 0.85\text{J/g}\cdot\text{K}, \text{ tensile strength} > 20\text{MPa}, \text{ tensile strength} > 20MP$
(http://fuxitech.gotoip3.com/)	$test\left(>R5/180^{\circ}\right)>3\times104\ times, electrical\ conductivity\ 5\times105\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for the conductivity\ 5\times105\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for the conductivity\ 5\times105\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for the conductivity\ 5\times105\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for the conductivity\ 5\times105\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for\ 5\times100\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for\ 5\times100\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for\ 5\times100\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for\ 5\times100\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for\ 5\times100\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for\ 5\times100\ S/m, heat\ resistance\ over 100\ hours\ testing\ 400^{\circ}\ Color for\ 5\times100\ S/m, heat\ resistance\ by 100^{\circ}\ Color\ for\ 5\times100\ S/m, h$
	Foam: Thermal conducting foam film, thickness 100 μ m, thermal conductivity 100–150 W/m·K, thermal diffusivity 800–900 mm ² /s, density 0.2 g/cm ³ , specific heat 0.85 J/g·K, heat resistance over 100 hours testing 400°C
Graphensic AB, Sweden (http://graphensic.com/shop/)	Film: Monolayer graphene on Si surface of 4H SiC semi-insulating substrate, size 2 inch, 7×7 mm ² or 15×15 mm ² , 100% covered
	Film: 4-inch graphene on silicon carbide wafers (SI or N-type), non-standard size samples, bi/few/multi-layer graphene, graphene on off-axis substrates, graphene on 6H or 3C silicon carbide, hydrogen-intercalated graphene, and graphene on C-surface

if graphene manufacturing companies could be more specific about the graphene materials being sold. Depending on the preparation methods, the industrial chains, including the providers of raw materials and the downstream businesses, are likely to be different. Such factors will influence the investment cycle, profit model(s) and competitive positions of the companies that are involved.

(ii) In addition to the applications listed above, many more graphene-related products have been proposed (some more examples are shown in Figs. 2e and f), although most of them are still in development. (However, one must note that not all of them have used the advantages of graphene materials and this has raised debate about the actual role of graphene in some of the products.) (iii) History has witnessed the rise and sustained use of many 'new' materials. Achieving stable mass production and a wide range of applications for new materials takes time. It will be of great interest to see how quickly graphene materials can penetrate into other commercial applications, in addition to further penetration into the applications that are being commercialized now and that are described in this article.

Finally, we would like to note that there is often a 'virtuous circle' or feedback loop between applied R&D and fundamental research. The intense efforts to commercialize graphene in suitable applications are already leading to observations during the course of such efforts, which spur on further work on the fundamental side. We expect this aspect of fundamental research on graphene and related materials

to also grow as a result of commercialization in existing and new areas.

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DECLARATIONS

YZ is a board member of The Sixth Element Materials Technology (Changzhou) Co. Ltd. HJ is the Chief Scientist of Wuxi Graphene Films Co. Ltd. RSR is the senior member of the Expert Advisory Committee of The Sixth Element Materials Technology (Changzhou) Co. Ltd. HMC's team has transferred its technology to set up the Deyang Carbonene Technology Co. Ltd.

Conflict of interest statement. None declared.

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100 | *Natl Sci Rev*, 2018, Vol. 5, No. 1

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