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石犬通訊

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Graphene

Graphene consists of a single layer of carbon atoms arranged in a two-dimensional honeycomb (hexagonal) lattice. Sheets of graphene stacked on top of each other are the basic 'building block' of graphite, which is commonly found as small flakes (generally <180 microns) in metamorphic rocks. Within a 1mm thick graphite flake there are approximately 3 million stacked graphene sheets spaced at 0.335nm and bonded weakly by van der Waals forces.

To avoid confusion the term graphene is generally used for graphite containing up to 10 sheets; because above this number the products and their properties are more reminiscent of graphite than graphene.

The history of graphene is relatively recent. In the late 1940s scientists studying thin graphite samples using electron microscopes observed layers in graphite flakes. However, it took until 1962 for the term graphene to be coined. This was by Hanns-Peter Boehm to describe the 'hypothetical' single-layer structure in extremely thin graphite samples he was researching. Over the next 40 years research continued but it was only in 2004 that Graphene was properly isolated and characterized by Andre Geim and Konstantin Novoselov from the University of Manchester in the UK. They used sticky tape to remove graphene flakes from the surface of graphite, transferring them onto a thin silicon dioxide layer on a silicon plate ('wafer"). The isolation of graphene won them the 2010 Nobel Prize for Physics.

Graphene has been described as a miracle material of the 21st Century because of its unique properties. It is the:

- thinnest compound known to man at one atom thick,
- lightest material known (with $1m^2$ weighing around 0.77 mg),
- strongest compound discovered (between 100-300 times stronger than steel),
- best conductor of heat at room temperature, and also the
- best conductor of electricity known.

Other notable properties are its uniform absorption of light across the visible and near-infrared parts of the spectrum and its potential suitability for use in electronic devices.

With these unique properties the potential of graphene in a range of products was recognized at an early stage and thousands of patents were taken out accordingly. Governments and Universities also spent vast sums of money in research and its use in defense for military applications was one such area.

Graphene Production

The two most established methods of graphene production are:

(1) Exfoliation – is where graphite layers are broken apart with the ultimate intention of yielding single-layer graphene sheets (aka "top-down" approach). There are several methods of which chemical exfoliation has been the most promising route for large

石墨烯

石墨烯由排列在二維蜂窩（六邊形）晶格中的單層碳原子組成。相互堆疊的石墨烯片是石墨的基本“構件”，通常在變質岩中以小薄片（通常<180 微米）的形式存在。在 1 毫米厚的石墨薄片內，大約有 300 萬個堆疊的石墨烯片，間距為 0.335 納米，並通過范德華力弱結合。

為避免混淆，術語“石墨烯”通常用於表示最多包含 10 個薄片的石墨；因為超過這個數字，產品和它們的特性更接近石墨而不是石墨烯。

石墨烯的歷史相對較短。在 1940 年代後期，科學家們使用電子顯微鏡研究薄石墨樣品，觀察石墨薄片中的層。然而，直到 1962 年，石墨烯這個詞才被創造出來。這是 Hanns-Peter Boehm 用來描述他正在研究的極薄石墨樣品中的“假設”單層結構。在接下來的 40 年裡，研究仍在繼續，但直到 2004 年，英國曼徹斯特大學的 Andre Geim 和 Konstantin Novoselov 才確切分離和表徵了石墨烯。他們使用粘膠帶從石墨表面分離石墨烯薄片，將它們轉移到矽板（“晶片”）上的薄二氧化矽層上。石墨烯的分離使他們獲得了 2010 年的諾貝爾物理學獎。

石墨烯因其獨特的特性被描述為 21 世紀的奇蹟材料。它是：

- 人類已知的最薄的化合物，只有一個原子厚，
- 已知最輕的材料（1 平方米重約 0.77 毫克），
- 已發現最強的化合物（比鋼強 100-300 倍），
- 室溫下最好的熱導體，也是
- 已知最好的電導體。

其他值得注意的特性是它對光譜的可見光和近紅外部分的光的均勻吸收以及它在電子設備中的潛在適用性。

憑藉這些獨特的特性，石墨烯在一系列產品中的潛力在早期就得到了認可，並因此獲得了數千項專利。政府和大學也在研究上花費了大量資金，其在國防軍事中的應用就是其中一個領域。

石墨烯的製造

石墨烯生產的兩種早期方法如下：

(1) 剝離 – 這裡石墨層被分解，最終目的是產生單層石墨烯片（又名“自上而下”的方法）。有幾種方法，其中化學剝離是最有希望大規模生產的途徑。最初使用氧氣，產生氧化石墨烯漿料。然後在該過程的第二階段通過受控還原去除氧氣以生產石墨烯。 另一種流行的方法是超聲波，在離心機中將石墨烯從石墨中分離。

(2) 外延 – 從碳原子生長石墨烯（又名“自下而上”的方法）。它利用廣泛使用的氣體如甲烷和苯 – 作為分子前體。在這種方法中，前體中的碳 - 碳鍵在高溫化學反應下分解。然後重新排列以形成沉積。一種廣泛使用的方法是在 1000°C 至 1100°C 的熱金屬基板（通常是銅或鎳）上進行化

scale synthesis. Oxygen is used initially, producing a slurry of graphene oxide. The oxygen is then removed at the second stage of the process through a controlled reduction to produce graphene. The other popular method is sonification where graphene is separated from graphite in a centrifuge.

(2) Epitaxy – is where graphene is grown from carbon atoms (aka "bottom-up" approach). It relies on widely available gases such as methane and benzene - a molecular precursor. In this approach the carbon-carbon bonds within the precursor decompose under a chemical reaction at high temperature. The bonds are then rearranged to form graphene sheets. An approach widely used is chemical vapour deposition ("CVD") onto a hot metal substrate at 1000°C to 1100°C – typically of copper or nickel. A key part of the process is to separate the graphene film from the substrate. This is typically done by first adding a polymer layer to the surface of the graphene and then using harsh chemical etchants to eat away the metal and leave the graphene sheet attached to the polymer.

Epitaxy has more technical challenges than exfoliation, such as preventing defects in the sheet, curling of the sheet, as well as contamination from the substrate. The graphene produced from epitaxy has a larger lateral size compared to graphene produced through exfoliation, but production is more costly. With exfoliation, graphene produced sheets tends to have small lateral size and defects in the sheets are often present. The sheets also tend to reagglomerate and stack up.

In recent years, there has been an increasing list of production techniques, although most would seem to be in development stages related to niche applications. Laser induced 3D methods converting polymer films into 3D graphene patterns is used for electronics, nanocomposites, energy storage and air filtration systems. Other methods include nanotube slicing, spin coating, intercalation and microwave assisted oxidation.

Typically, there are three main types of graphene available commercially:

1. Small, exfoliated flakes, less than 5mm^2 in area.
2. Dispersions and solutions of graphene powders and flakes.
3. Large sheets (up to 15cm in diameter) produced epitaxially.

Characterisation of Graphene and Standardisation

There is no measurement technique that can determine all of the material properties and so complimentary techniques are required for either chemical or physical characterisation. The following are the parameters which typically define the product.

- Chemical Composition – percentages of carbon and impurities.
- Surface Area – reported as surface area over mass (m^2/g). A higher surface area graphene has a higher capacitance.
- Flake / grain size – typically the lateral size of the graphene flakes
- Electrical Conductivity – is the ability to conduct electricity measured in Siemen's per length (either S/m or S/cm).
- D/G ratio – is a measure of how perfect is the graphene – if the D to G ratio is small the less defective is the structure. There is a second order band which implies the number of layers of graphene.

As there are still many different types of graphene available, where the type maybe suitable for certain applications and not others, reliable material characterization is extremely important. For example, for graphene flakes sold as powder or dispersion, the lateral size and thickness will impact on whether the material is better for applications such as composites or energy storage. Furthermore, for commercially produced graphene, physical measurands such as size distribution can have a broad range that must be fully understood and not just quoted as an average value. It is therefore hard to present a standard form of graphene.

To help overcome this, the first adoption of graphene standards *ISO/TS*

學氣相沉積（"CVD"）。一個關鍵步驟是將石墨烯薄膜與基板分離。這通常是先在石墨烯表面添加聚合物層，然後使用苛刻的化學蝕刻劑腐蝕金屬使石墨烯片附著在聚合物上來完成的。

外延比剝離具有更多的技術挑戰，例如在沉積過程中防止石墨烯的缺陷、捲曲以及來自基板的污染。與通過剝離工藝生產的石墨烯相比，生產的石墨烯具有更大的橫向尺寸，但生產成本更高。通過剝離石墨烯生產的片材往往具有較小的橫向尺寸，並且片材中常存在缺陷。此外，這些片材往往會重新團聚並堆疊起來。

近年來，生產技術的方法越來越多，儘管大多數似乎處於與應用相關的開發階段。激光誘導 3D 方法將聚合物薄膜轉化為 3D 石墨烯圖案，用於電子產品、納米複合材料、能量存儲和空氣過濾系統。其他方法包括納米管切片、旋塗、嵌入和微波輔助氧化。

市面上普遍有三種主要類型的石墨烯。

1. 剝落的小薄片，面積小於 5mm^2。
2. 石墨烯粉末和薄片的分散體和溶液
3. 外延生產直徑達 15 厘米的大面積片材。

石墨烯的參數和表徵

沒有可以測量材料所有特性的技術，因此化學或物理表徵都需要技術互補。 以下是通常定義產品的參數。

- 化學成分 – 碳和雜質的百分比。
- 表面積 – 報告為表面積與質量 (m^2/g)。更高表面積的石墨烯具有更高的電容。
- 尺寸 – 通常是石墨烯薄片的橫向尺寸
- E.C（電導率）- 是以西門子每單位長度（S/m 或 S/cm）衡量的導電能力。
- D/G 比率 – 衡量石墨烯的完美程度——如果 D 與 G 的比率小，則結構缺陷越少。有一個二階帶，暗示著石墨烯的層數。

由於仍有許多不同類型的石墨烯可用，其中的類型可能適用於某些應用而不是其他應用，因此可靠的材料表徵極其重要。例如，對於作為粉末或分散體出售的石墨烯薄片，橫向尺寸和厚度將影響材料是否更適合複合材料或儲能等應用。此外，對於商業生產的石墨烯，尺寸分佈等物理測量可以具有廣泛的範圍，必須充分理解，而不僅僅是作為平均值引用。因此，很難提出標準形式的石墨烯。

為了幫助克服這一問題，石墨烯標準 *ISO/TS 80004-13:2017 – 詞彙 – 石墨烯和相關二維 (2D) 材料* – 於 2017 年 9 月以不同形式的 ISO 術語標準的形式實現石墨烯。

2021 年 3 月，納米技術標準公佈了 *ISO/TS 21356-1:2021*，用於測量石墨烯的結構特性，通常以粉末或液體分散體的形式出售。通過標準化方法，可以一致地測量石墨烯的物理特性，例如橫向薄片大小、薄片厚度、無序程度和比表面積，並允許最終用戶比較不同的石墨烯產品並選擇合適的產品加入到最終的商業產品，如復合材料、電池或電子產品。

石墨烯市場展望

除了降低成本及投資回報之外，該行業還面臨著相互關聯的挑戰，例如潛在客戶認為不成熟的看法（過往新材料需要多年才能被商業

80004-13:2017 – Vocabulary – Graphene and related two-dimensional (2D) materials - was realized in September 2017, in the form of an ISO terminology standard for the different forms of graphene.

In March 2021, the nanotechnologies standards have announced *ISO/TS 21356-1:2021* for measuring the structural properties of graphene, typically sold as powders or in a liquid dispersion. Through standardized methods, the physical properties of graphene, such as lateral flake size, flake thickness, level of disorder and specific surface area, could be measured consistently and allow end-users to compare different graphene products and choose the right one to incorporate in the final commercial products such as composite, batteries or electronics.

Market Outlook

Beyond cost reduction and investment return the industry still faces interrelated challenges such as the perception of immaturity (historically new materials take years to be accepted commercially) among potential customers; lack of standardization; and, regulatory hurdles. Also, the capability to provide either powders on the one tonne/yr scale or substrates at thousands of m^2/yr leads to problems in reproducibility.

From a consumer viewpoint the potential of graphene has been demonstrated in prototypes developed by different companies for products such as anti-corrosion coatings, supercapacitors, heat management devices for electronics, biomedical sensors, lightning strike protection and printed electronics. Furthermore, graphene has been incorporated into niche products such as sports equipment, bikes, and supercars. In EV batteries graphene anodes can charge and discharge 10 times faster than conventional graphite.

Over the next 5 years rapid industrialization and increasing demand for lightweight, flexible and renewable materials across the globe are among the key factors driving the market growth. Graphene is used to enhance the physical properties of various polymer materials, including natural and synthetic rubber, thermoplastic and thermoset composites, paints, coating, and elastomers. Graphene films are being increasingly utilized in the manufacturing of protective coatings on flexible electronic devices.

Other factors, including extensive research and development activities to improve the thermal and electrical conductivity properties, along with immense utilization of graphene for manufacturing lightweight sports equipment, are projected to drive the market further. Looking forward, the global graphene market is expected to grow at a CAGR of around 30% during 2021-2026 (Source: IMARC Group).

Price of Graphene

A review of online market websites such as Alibaba show a whole of range of graphene products and prices. Many of these will contain graphene but in small quantities. Many may in fact be graphite.

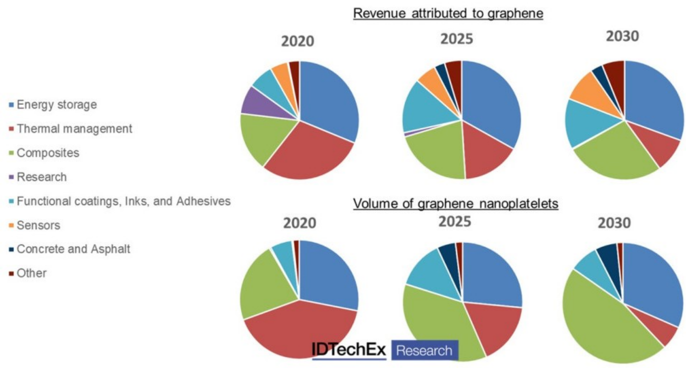
Where there is graphene powder the range is high from US$1.50/gm to US$350/gm. The quality of graphene is not stated and to protect competitive advantages sellers often have strict non-disclosure measures. For monolayer CVD produced graphene on copper, UK listed company Graphenea were quoting US$396 for 15cm x 15cm sheets.

接受）；缺乏標準化； 監管障礙。此外，提供每年 1 噸規模的粉末或每年數千平方米的生產能力或會導致質量問題。

從消費者的角度來看，石墨烯的潛力已經在不同公司為產品開發的原型中得到了證明，這些產品包括防腐塗層、超級電容器、電子熱管理設備、生物醫學傳感器、雷擊保護和印刷電子產品。此外，石墨烯已被納入小眾產品，如運動器材、自行車和超級跑車。在電動汽車電池中，石墨烯陽極的充電和放電速度比傳統石墨快 10 倍。

在未來的 5 年中，全球對輕質、柔性和可再生材料的快速工業化和日益增長的需求是推動市場增長的關鍵因素。納米技術在電子行業中的整合也起到了推動作用。石墨烯用於增強各種聚合物材料的物理性能，包括天然和合成橡膠、熱塑性和熱固性複合材料、油漆、塗料和彈性體。石墨烯薄膜越來越多地用於製造柔性電子設備的保護塗層。

其他因素，包括廣泛的研究和開發活動，以提高導熱性和導電性，以及石墨烯在製造輕型運動設備方面的大量利用，預計將進一步推動市場發展。展望未來，全球石墨烯市場預計將在 2021-2026 年間以 30% 左右的複合年增長率增長（來源： IMARC Group）。



Graphene market forecast (Source: IDTechEx)
石墨烯市場預測 (來源 ： IDTechEx)

石墨烯價格

據阿里巴巴等在線市場網站的評論顯示了一系列石墨烯產品和價格。其中許多將包含石墨烯，但數量很少。許多實際上可能是石墨。

在有石墨烯粉末的地方，價格範圍大，從每克 1.50 美元到每克 350 美元。石墨烯的質量沒有說明，為了保護競爭優勢，賣家通常有嚴格的保密措施。 而英國上市公司 Graphenea 通過 CVD 生產的 15cm x 15cm 單層銅基石墨烯的報價為 396 歐元。

Rockhound is a HK based company set up to serve the minerals industry in the Region. The company offers technical valuations and services in the natural resources sector.

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MHKIE – Member of the Hong Kong Institute of Engineers
MCIM – Member of the Canadian Institute of Mining and Petroleum

烯石電動汽車新材料控股有限公司
Graphex Group Limited (6128.HK)

集團的主要業務為在香港及中國內地從事景觀設計，在中國內地及意大利從事餐飲業務以及在中國內地從事石墨烯業務。

石墨烯業務佔集團收入的主要部分。截至二零二零年十二月三十一日止年度，石墨烯分部貢獻收入215.5百萬港元，佔集團總收入55.4%，經調整EBITDA約49.7百萬港元，相當於集團EBITDA 總額58.5%。該業務的毛利率為27.4%及經調整EBITDA利率為23.1%。

石墨烯分部的主要產品為球形石墨。球形石墨也稱為電池級石墨(battery-grade graphite)，是用於生產鋰離子電池的石墨電極的重要電池製造材料。集團將片狀石墨加工成超高純度（大於99.95%）的微觀球體，其顆粒分佈尺寸(D50) 為10-15微米。其微觀均勻的球體可使電池製造商將石墨的體積壓縮至更小，從而生產出更緻密、更高效的石墨電極。集團目前每年生產約10,000公噸球形石墨。

鋰離子電池的需求源自電動及混合動力汽車，並各自可作為風能及太陽能可再生能源發電場的儲存解決方案。分析師預測，未來十年電動汽車銷量的複合年增長率為29%。預計全球電動汽車的銷量將從二零二零年的2.5百萬輛增長至二零二五年的11.2百萬輛，到二零三零年增長近三倍達到31.1百萬輛。到二零三零年，預計電動車將佔新能源車銷售總市場份額約32%。分析師預計，到二零三零年中國佔全球電動市場的49%，歐洲佔27%及美國佔14%。

由於每輛電動汽車消耗約70千克球形石墨。預計到二零二三年，集團產品將供不應求。集團正準備透過擴大製造產能以利用該需求增長，並制定戰略計劃，在未來三年內將集團的產能從10,000公噸提升至40,000公噸。此外，結合專有的球形石墨加工知識及25項專利（其中9項專利於二零二零年獲得），集團認為集團擁有強大的競爭優勢。

Directa Plus says new research supports the use of its graphene nano-materials in COVID face masks (excerpt)

13 Jul 2021 <Graphene-info>

Directa Plus recently stated that a research paper has been published in the journal iScience, supporting the use of its ‘functionalized’ graphene as an antimicrobial material in face masks.

The peer-reviewed paper said the company's G+ nanomaterials and those from graphene oxide provide a “critical opportunity to significantly increase face mask efficacy”.

Directa said to date it has treated and supplied more than 240,000 meters of G+ graphene fabrics and produced and delivered more than one million G+ filters to fight the COVID-19 pandemic.

In March 2021, Directa Plus also received positive test results confirming that its graphene nanoplatelets are not absorbed through human skin. The Company said this was the eighth in vitro test to show that there is no absorption potential for the Pure G+ powder.

新發明石墨烯薄膜有效保護畫作 (節錄) 2021年7月15日<大紀元>

藝術畫作中使用的顏料在氧化劑存在的情況下，暴露於紫外線和可見光下會降解、褪色或發黃。這對畫作造成無法修復的傷害。

現有的方法給畫作刷上一層作為保護的清漆，效果並不好，因為要除掉這層保護漆需要用到某些溶劑，會影響保護漆之下的顏料層。希臘希臘帕特雷大學（University of Patras）和意大利佛羅倫薩大學（University of Florence）合作的一份研究提出一個有創意的想法，使用一層石墨烯薄膜作為保護層。

在實驗室的檢測結果顯示，這層薄膜不怕潮濕、氧化劑或任何有害污染物的侵襲，還能吸收大量有害的紫外線。最後，和其它保護方法相比，石墨烯薄膜較容易移除，而不會傷害畫作。

'Wonder material' used to detect SARS-CoV-2 virus in laboratory experiments (excerpt)

16 Jun 2021 <News-Medical.net>

Researchers at the University of Illinois Chicago have successfully used graphene -- one of the strongest, thinnest known materials -- to detect the SARS-CoV-2 virus in laboratory experiments. The researchers say the discovery could be a breakthrough in coronavirus detection, with potential applications in the fight against COVID-19 and its variants.

In experiments, researchers combined sheets of graphene, which are more than 1,000 times thinner than a postage stamp, with an antibody designed to target the infamous spike protein on the coronavirus. They then measured the atomic-level vibrations of these graphene sheets when exposed to COVID-positive and COVID-negative samples in artificial saliva. These sheets were also tested in the presence of other coronaviruses, like Middle East respiratory syndrome, or MERS-CoV.

The UIC researchers found that the vibrations of the antibody-coupled graphene sheet changed when treated with a COVID-positive sample, but not when treated with a COVID-negative sample or with other coronaviruses. Vibrational changes, measured with a device called a Raman spectrometer, were evident in under five minutes.

Developing lactose-free milk with graphene oxide based nano filtration membranes (excerpt) 13 Jul 2021 <Phys.org>

Over the past years, graphene oxide membranes have been mainly studied for water desalination and dye separation. However, membranes have a wide range of applications, such as within the food industry. A research group led by Aaron Morelos-Gomez of Shinshu University's Global Aqua Innovation Center investigated the application of graphene oxide membranes for milk, which typically creates dense foulant layers on polymeric membranes.