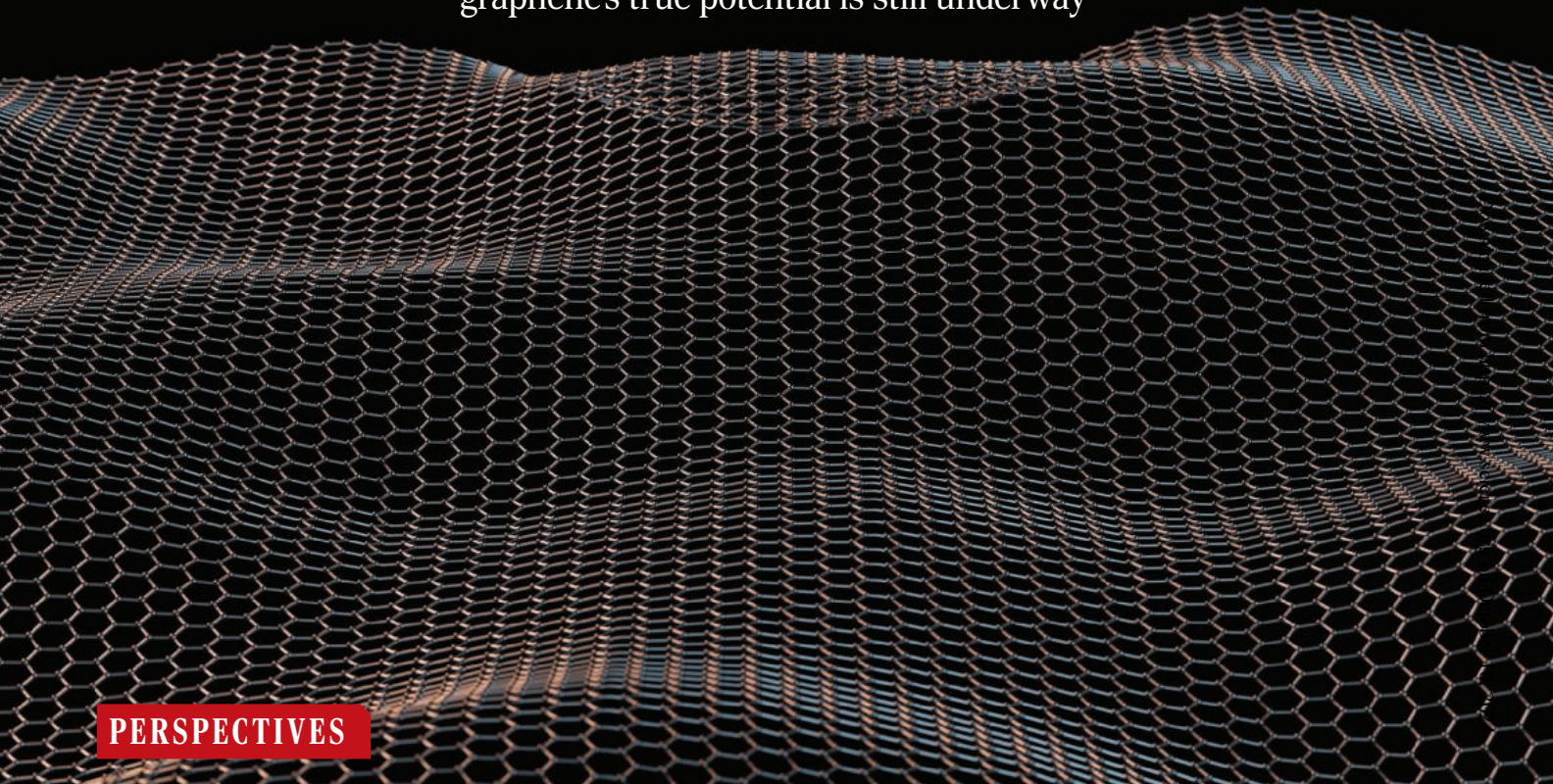Check for updates

LANDMARK: GRAPHENE

Graphene, beyond lab benches

Twenty years since its discovery, the journey to reach graphene's true potential is still underway

PERSPECTIVES

By **Yixuan Zhao**[1,2,3] and **Li Lin**[1,2]

Twenty years after the discovery of graphene—a one-atom-thick layer of carbon atoms in a honeycomb structure (1)—research on this remarkable material has evolved from benchtops to large-scale productions and commercial applications. Graphene is known for its breadth of exotic properties, including electrical conductivity up to 70% higher than that of copper, thermal conductivity at room temperature that is more than twice that of pyrolytic graphite, and strength that is 200 times as great as that of steel (at one-sixth the weight). These attributes make graphene and its derivatives ideal for a myriad of uses, including electronic, structural, and biomedical uses. However, even broader industrial applications of graphene are yet to be realized.

As described in the 2004 pioneering paper by Novoselov *et al.* (1), a highly oriented pyrolytic graphite is mechanically exfoliated to produce monolayer graphene flake using an adhesive tape. The new material exhibits intriguing properties. The authors observed a strong ambipolar electric field effect—an ability to switch between positive and negative charges upon an applied gate voltage. They also noted high room temperature carrier mobilities, which are associated with how fast an electron or a hole moves through a material. These properties make graphene promising for electronic applications. Although the mechanical peeling process produced pristine graphene, it only made small flakes with sizes ranging from a few tens to hundreds of micrometers. Thus, early graphene research focused on synthesizing high-quality monolayer or multilayers of graphene in a continuous form, primarily by chemical vapor deposition on metal substrates using carbon-containing precursors. However, limited scale of production, a large variation in the quality across different batches, and a lack of reliable methods to transfer graphene from one substrate to another have slowed down the application of high-quality

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graphene films for electronic devices.

The initial focus of graphene research and commercialization centered on its derivatives, such as graphene nanoplatelets (two-dimensional particles made of stacked sheets), graphene oxides with functional oxygen groups, and reduced graphene oxides in which the oxygen groups are removed (see the figure). These are relatively easier to produce in large quantities than the pristine counterpart, which is produced primarily by exfoliating graphite mechanically by an adhesive tape, but produce a large amount of defects within the product (2). Thus, potential applications of graphene have switched toward those that can tolerate structural imperfections but still benefit from the strength and light weight of graphene derivatives, such as composites, coatings, and reinforcements. For example, graphene nanoplatelets have been used in anticorrosion coating, fire retardants, and electromagnetic shielding materials, which are all close to commercialization (3). Additionally, the sufficiently high conductivity, electrochemical stability, and porous structure give graphene derivatives the potential to be used for energy storage and conversion devices.

By contrast, industry application of high-quality, continuous graphene is still in the rudimentary stage. Electronic and optoelectronic devices require the synthesis of large-scale uniform monolayer or multilayer graphene films with sufficiently high carrier mobilities (usually above 10,000 cm^2/Vs). Laboratory- and industry-scale efforts have been devoted to optimizing the chemical vapor deposition–based growth process of graphene to reduce the overall defect density as well as the number of grain boundaries and wrinkles, which impede electrical transport. In addition, side reactions occur on the graphene surface during a large-scale production, such as the formation of amorphous carbons, which alter the intrinsic properties of graphene. Metal substrates, such as copper foils, have been widely used for growing large-are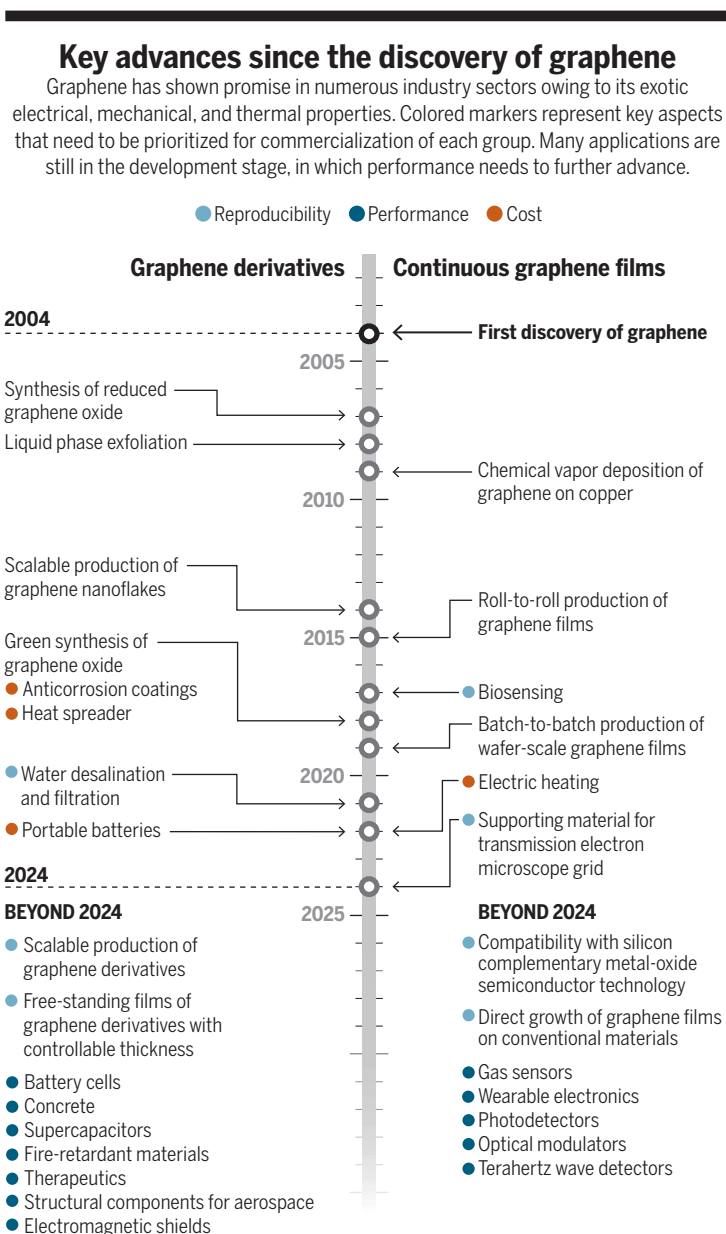a monolayer graphene films. A surface-mediated growth mechanism, in which a further growth of additional layers is hindered by the reduced catalytic activity of the substrates with graphene coverage (4), enables fine control over the film thickness. Currently, wafer-scale growth of single-crystalline graphene film with reduced density of grain boundaries has only been achieved on metals (5). Additionally, depositing graphene films on nonmetal substrates, such as semiconductors and insulators, is desired for a broader scope of electronic and photonic devices. Chemical vapor deposition growth of graphene on insulating sapphire substrates has been demonstrated recently (6), moving graphene a step closer to commercial electronic and optoelectronic device application. The carrier mobility of chemical vapor deposition–produced graphene of more than 1 million cm^2/Vs suggests that the gap between laboratory-grown and pristine graphene no longer exists (7). However, the reported laboratory-scale devices are based on a carefully selected area within a large graphene-coated substrate and thus suffer from considerable device-to-device variations.

From the perspective of electronic applications, the compatibilities of chemical vapor deposition graphene with the existing microfabrication facilities and techniques for silicon-based complementary metal-oxide semiconductor technologies is critical. Unfortunately, conformal growth of graphene on silicon/silicon dioxide substrates is difficult owing to the formation of impurities, such as carbides, during the growth process (8). In addition, amorphous silicon substrates cannot decompose carbon-containing precursors, resulting in high defect density of graphene films. Catalytic capacity has been improved by introducing gas-phase metal catalysts (8), but optimizing the growth parameter for large-scale production of graphene on silicon substrates is still challenging.

One solution to circumvent the challenges with silicon substrates is to grow graphene on a separate substrate and then transfer it onto a silicon surface. However, this approach often produces cracks, wrinkles, folding of graphene sheets, and other defects, which create large device-to-device variations and affect the production yield. These imperfections also alter integration of dielectrics onto graphene. Because dielectrics are electrical charge–storing materials with high electrical resistivity, they dictate the electronic performances and working stabilities of graphene-based electronics. Poor graphene-dielectric interfaces that are contaminated by transfer-related residues and pinholes (a type of defect in electronics) deteriorate the carrier mobility of graphene films. With device miniaturization, even a small defect can severely deteriorate performance.

Many strategies have been developed to suppress the transfer-induced imperfections and to improve dielec-

Key advances since the discovery of graphene

Graphene has shown promise in numerous industry sectors owing to its exotic electrical, mechanical, and thermal properties. Colored markers represent key aspects that need to be prioritized for commercialization of each group. Many applications are still in the development stage, in which performance needs to further advance.

● Reproducibility　● Performance　● Cost

Graphene derivatives　　**Continuous graphene films**

2004 — First discovery of graphene

2005
Synthesis of reduced graphene oxide
Liquid phase exfoliation

Chemical vapor deposition of graphene on copper

2010
Scalable production of graphene nanoflakes

Roll-to-roll production of graphene films

2015
Green synthesis of graphene oxide
● Anticorrosion coatings
● Heat spreader

● Biosensing
Batch-to-batch production of wafer-scale graphene films

● Water desalination and filtration
2020
● Portable batteries

● Electric heating
● Supporting material for transmission electron microscope grid

2024

BEYOND 2024
2025
● Scalable production of graphene derivatives

● Free-standing films of graphene derivatives with controllable thickness

● Battery cells
● Concrete
● Supercapacitors
● Fire-retardant materials
● Therapeutics
● Structural components for aerospace
● Electromagnetic shields

BEYOND 2024
● Compatibility with silicon complementary metal-oxide semiconductor technology

● Direct growth of graphene films on conventional materials

● Gas sensors
● Wearable electronics
● Photodetectors
● Optical modulators
● Terahertz wave detectors

tric integration. Controlling delamination and lamination forces and avoiding implanting trace impurities on the surface have helped in mitigating the defects (9). Current silicon technologies also give hints as to how to create these processes. For example, a conventional wafer bonding process has been adopted to directly bond graphene grown on copper substrates onto a desired substrate with an adhesive layer between them followed by the removal of the copper layer by chemical etching (10). Another approach facilitates the transfer of graphene without cracks by controlling the adhesion between tape and graphene by ultraviolet light illumination (11). Moreover, van der Waals layered dielectric materials, such as hexagonal boron nitride (hBN) and bismuth selenate (Bi_2SeO_5) (12), can be used as supporting layers to assist with transferring and to avoid interfacial contaminations.

Nevertheless, these techniques have only been tested at laboratory scale, and careful testing at industry scale is needed. To avoid heavy investments in building new processes and facilities to mass-produce graphene products, it is essential to develop procedures that are compatible with the current manufacturing processes. Further, transfer of large-area graphene films requires repeatability at production capacity. Integrating automatic transfer processes, using robotics and machine designs, into the existing semiconductor facilities can improve consistency. At the same time, developing methods to directly grow graphene films on conventional substrate materials bypasses transfer-related problems and can help accelerate commercialization (13). Thus, commercialization of graphene-based products primarily relies on collaboration between academia and industry.

A major challenge in commercializing graphene and its derivatives is the high production cost for the limited production volume. Raw materials, such as methane gas or raw graphite powders, only account for a small proportion of the overall cost. Rather, equipment designs for large-scale batch production and processing of synthesized graphene account for most of the initial investment. Thus, the industry is driven toward high-margin applications that require less investment for substantial performance improvement over existing products. This has led to faster commercialization of graphene derivatives for various structural components compared with high-quality graphene films for devices. For example, graphene in transparent conductive films has been hindered by its high production cost compared with the conventional indium tin oxide. Even the graphene derivatives that have already been commercialized or are close to commercial

applications need to be further developed to reduce cost. The current mainstream methods of producing graphene nanoplatelet films are filtration and layer-by-layer assembly using electrostatic interaction, which are slow and not ideal for mass production. Reducing costs without deteriorating its properties is crucial for graphene products to break into the market.

Variations in production methods across industry result in a substantial difference in the properties and performance of graphene products. This highlights the need for developing standards for graphene and its derivatives. With this, the development of high-throughput characterization is crucial for measuring the properties to sort out those that do not meet the standards. Optical characterization methods, such as ellipsometry contrast microscopy and terahertz time-domain spectroscopy, can inspect large-area graphene rapidly (14). However, some detrimental structural defects can only be examined using advanced microscopy, which are generally time-consuming. Automatic characterization combined with machine learning and artificial intelligence can help overcome the limitation. For instance, automated imaging and data analytics can find features that represent defects with minimal human contribution (15).

There is still a substantial gap between academia and demands from the industry. Closer collaboration to reduce this gap is required. Particularly, a comprehensive system of standards should include application-related grades for guiding the products and their entry into specific markets, such as specific properties for specific functions and corresponding measurement methodologies. These standards should be drafted through collaborations between researchers, manufacturing companies, and application enterprises. ∎

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NEURODEVELOPMENT

Genomic patterns in the schizophrenia brain

Somatic noncoding mutations likely contribute to schizophrenia development

By **Joon-Yong An**[1,2,3] *and* **Yujin Kim**[2,3]

Human germline mutations—genetic changes in an egg or sperm—are inherited, present in every cell, and play roles in early development (1), whereas somatic mutations arise postzygotically and may or may not affect developmental trajectories. Neurons accumulate hundreds to thousands of somatic mutations throughout development, with distinct mutational processes and rates occurring at various developmental stages (2). Whole-genome sequencing studies characterizing somatic mosaicism in early human brain development indicate that the mutation rate is relatively low during early pregastrulation (the first 2 weeks after fertilization) but increases substantially during late neurogenesis in the prenatal period (starting at 22 weeks of gestation), primarily owing to oxidative damage (3). On page 217 of this issue, Maury *et al.* (4) report that somatic mutations in the brains of individuals with schizophrenia occurred during neogenesis. This suggests that intrauterine factors might influence mutational mechanisms and brain development in utero.

Somatic mutations in the human brain are not evenly distributed across the genome but accumulate in regions implicated in neurodevelopmental and neuropsychiatric disorders (5–7). Protein-altering somatic mutations in the brains of individuals with schizophrenia or autism often occur in the same genes that are affected by

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