



A decade of graphene research: production, applications and outlook

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Graphene research has accelerated exponentially since 2004 when graphene was isolated and characterized for the first time utilizing the ‘Scotch Tape’ method by Geim and Novoselov and given the reports of unique electronic properties that followed. The number of academic publications reporting the use of graphene was so substantial in 2013 that it equates to over 40 publications per day. With such an enormous interest in graphene it is imperative for both experts and the layman to keep up with both current graphene technology and the history of graphene technology. Consequently, this review addresses the latter point, with a primary focus upon disseminating graphene research with a more applicatory approach and the addition of our own personal graphene perspectives; the future outlook of graphene is also considered.

Introduction

The world of materials research is currently engulfed by research focusing on the mass production, characterization and real-world applications of ultra-thin carbon films [1–10]; the thinnest of which is graphene. Research groups across the globe are currently devoting significant attention to graphene in the hope of discovering an application worthy of the high street. Nearly a decade of graphene research has promised potential applications including longer-lasting batteries [11], more efficient solar cells [12], corrosion prevention [13], circuit boards [14], display panels [15], and medicinal technologies such as the point-of-care detection of diseases [16]; so it comes as no surprise that there are many scientists eager to make the significant breakthrough which could be commercially exploited and implemented into everyday life. So, what is graphene and why has all this fuss about it been created? What makes graphene so special as to inspire the interest of governments, such as the British government, who have invested over 20 million GBP into graphene-related research [17]. Having seen governments back projects that have not yet benefited their countries (such as the human genome project), are governments not taking a huge

risk with tax-payer’s money once again in the hope of developing futuristic technologies with graphene? Two decades ago carbon nanotubes, a sister material of graphene, were reported to have many real-world applications and yet to this day there is little in the way of commercial use. So what makes graphene different? We hope to answer such questions in this short review, by way of explaining the plethora of potential benefits graphene exhibits, based upon current theoretical observations.

Furthermore this review aims to offer a basic background of graphene, discuss some existing research regarding graphene and offer our own perspective and insight into the tough questions asked in this opening gambit. One hopes that the intense research ploughed into graphene will return more real-world applications than its sister material carbon nanotubes, for instance, which since their discovery (the discovery date and discoverer remains contentious [18]) have been utilized very little in real-world applications (however, a recent report has detailed the fabrication of a carbon nanotube-based computer chip [19]) despite the promising properties of a remarkably high tensile strength and conductivity [20]. However, as excitable as the graphene revolution has been for scientists, it remains to be seen whether this ‘wonder material’ will go on to reach the vast potential expected from it.

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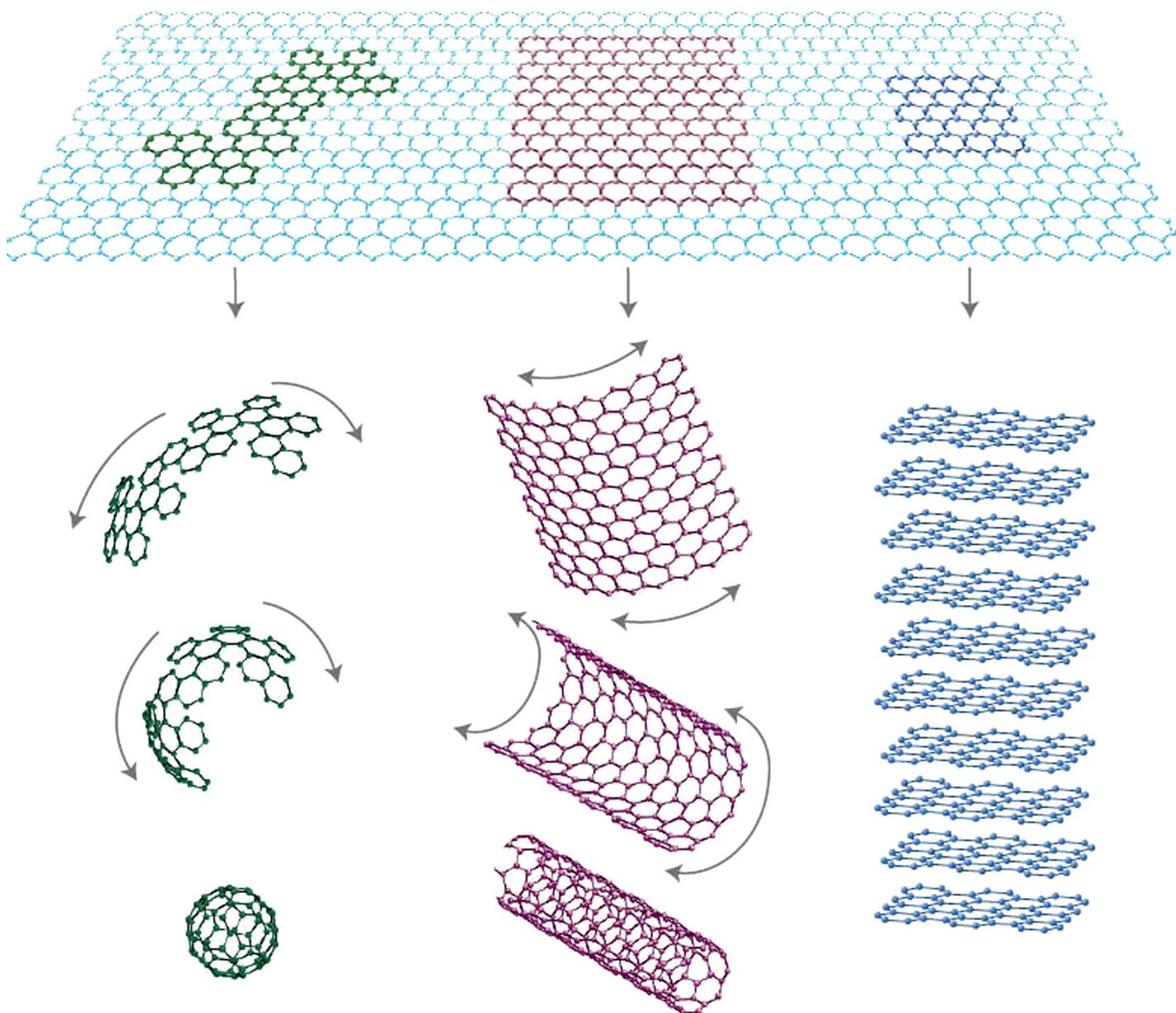


FIGURE 1

Graphene (top) and related structures: fullerene (bottom left); carbon nanotubes (bottom centre); and graphite (bottom right). Image reproduced from Ref. [22] with permission from Nature.

Structure, synthesis and properties

Graphene (Fig. 1) is a hexagonal structure consisting of sp^2 hybridized carbon atoms [21], described by some as the ‘mother’ [22] of all graphitic carbon materials due to it essentially being *the* building block for carbon nanotubes (effectively ‘rolled up’ graphene sheets) and graphite (stacked graphene sheets held together by strong Van der Waal’s forces). Graphene leapt to prominence during the mid-2000s when Geim and Novolosev isolated and characterized pristine graphene (with no heteroatomic contamination) [10] for the first time utilizing the now widely accepted terminology ‘Scotch Tape method’ [23]; which is affectionately known as a remarkably simple way to isolate graphene. Briefly, this method involves using a piece of adhesive tape to remove flakes of graphite from a slab of highly ordered pyrolytic graphite (HOPG), which are subsequently deposited upon a silica slide (Fig. 2).

Thereon, the flakes are exfoliated using more adhesive tape and applied to further silica slides until finally a one atom thick layer of graphite, *viz.* graphene, is left immobilized upon the slide [23]. This breakthrough of easily isolating graphene allowed graphene’s unique properties to be measured and quantified, such as reporting that graphene exhibits a remarkable high charge-carrier mobility of $2000\text{--}5000\text{ cm}^2/\text{V s}$ [23]. This was not however the first time ultra-thin carbon films had been observed; in fact there were plenty of reports prior to 2005 where even monolayer graphene was observed but researchers failed to identify any of its unique properties [10,24–26]. For instance, graphite oxide was independently synthesized in the late 1950s by Hummers [27], in 1898 by Staudenmaier [28], and prior to this in 1859 by Brodie [29]. There were reports of chemically reduced graphene oxides by 1962 [30], and even synthesis of monolayer graphene using silicon carbide

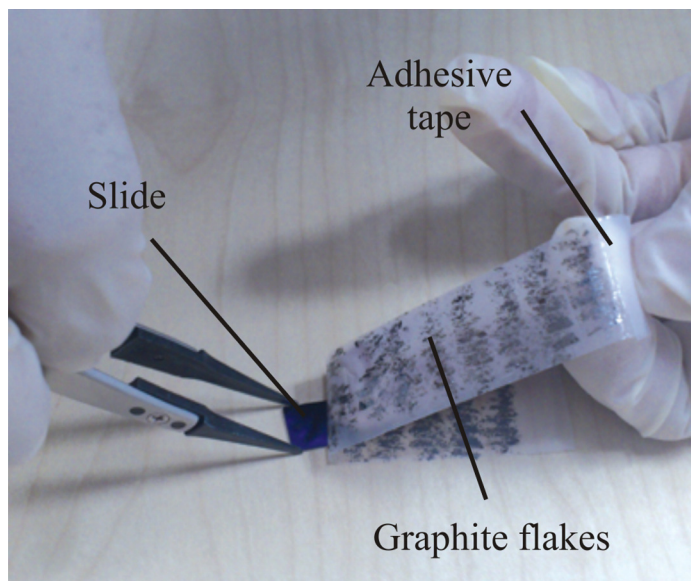


FIGURE 2

'Scotch tape' procedure, reported by Novoselov and Geim in 2004. Picture adapted from Ref. [86] with permission from Nature.

substrates was achieved by 1975 [31]. However, none of the above reports discovered/reported the unique properties of graphene; hence it was the combination of the simple isolation strategy *and* the discovery of the unique properties which kick-started the engine that is now graphene research for futuristic technologies [10]. The authors (Geim and Novoselov) were duly awarded the Nobel Prize for physics in 2010 for their pioneering work regarding two-dimensional atomic crystals [32].

Since the aforementioned work, the focus for some turned to exploring the large-scale synthesis of graphene, others to manipulating the structure in a manner that could yield beneficial changes in its properties, or continue to discover the physical characteristics of graphene as Geim and Novoselov continue to do. The method of production quickly became a pertinent problem with graphene as the original adhesive tape method can only isolate small amounts of graphene and is a laborious process. The large-scale synthesis of graphene emerged as a much-needed solution, which in truth has still not been properly addressed/refined nearly a decade later. The current methods of large-scale graphene synthesis include many variations of the so-called 'Hummers' method, devised by William Hummers in the late 1950s [27]. The method utilizes powerful oxidizing agents and strong acids to strip apart the graphene layers from a source of graphite – usually a high grade graphite powder available from any good chemical supplier. However, as this method creates *graphene oxide*, it is necessary to reduce the graphene oxide further to create graphene, termed reduced graphene oxide, which depending on the success of the reduction process can yield near fully reduced graphene oxide (*viz.* graphene, usually termed *rGO*) or partially reduced graphene oxide. Such reduction approaches can be thermal [33] or chemical [34] in nature and there are many other approaches available. Perhaps the best example to date of a chemically reduced graphene was presented in 2008 by Tung et al., who cleverly exploited the powerful reducing ability of hydrazine by immersing graphene oxide paper in pure hydrazine [35]. Reportedly, after a

few hours the paper disappears to leave a suspension of hydrazine with graphene platelets dispersed within. The graphene/hydrazine suspension can be spin-coated upon a substrate such as silica for characterization. Clearly there are safety concerns with hydrazine, which the authors have addressed by reporting that the graphene can subsequently be transferred to an organic solvent such as DMSO. There are questions over the mono-dispersity of graphene platelets and the number of layers given that, although the authors report high levels of monolayer graphene, in reality it is hard to imagine this to be the case throughout an entire batch due to inevitable flocculation and coalescence. Other graphene production methods exist but are lesser used, including methods to produce up to 30 square inches of graphene [36]. These include ion implantation [37], chemical vapour deposition (CVD) [36,38], liquid-phase exfoliation [39,40], and epitaxial growth upon a silicon carbide substrate [41]. Such methods and many more are discussed further in Novoselov's paper entitled 'A Roadmap for Graphene' [9]. As of 2013, graphene grown *via* CVD methods were shown to Exhibit 90% of the theoretical strength of pristine graphene, according to Lee et al. [42].

Since the *graphene revolution* commenced there has been an enormous amount of continuing work into the investigation of graphene's physical properties. Mentioned previously was the charge carrier mobility of graphene being exceedingly high, in the region of 2000–5000 cm²/V s [23]. Since those early reports, the charge carrier mobility of suspended graphene solutions has been shown, under optimal conditions, to exhibit charge carrier mobilities in excess of 200 000 cm²/V s [21,43,44]. The implications of such a highly permitting electron transport material are potentially profound in applications such as field effect transistors (FETs), which, even as of 2010, could operate at frequencies as high as 100 GHz [45]; and more recently graphene FETs can operate at terahertz frequencies [46]. Graphene also offers a tremendously high optical transparency of up to 97.7% [10] (or conversely, low optical absorptivity for a monolayer of 2.3%) [47]. Such characteristics have potential benefits for transparent electrodes in solar cell applications [48] and even holographic data storage [49]. Other properties include a high thermal conductivity of 5000 W m⁻¹ K⁻¹ [50], a high Young's modulus of ~1 TPa [51], and extraordinarily large specific surface area of 2630 m² g⁻¹ [52]. Instead of discussing the physical properties in detail, we have provided some reviews for interested readers to refer to in Refs. [10,21,52]; the remainder of this paper shall instead focus on the exciting applications ahead for graphene.

Graphene applications

Since 2004, the number of graphene-related academic publications has substantially increased. Fig. 3 illustrates the surge in graphene as well as reporting some historical points of interest; there were over 14,000 papers published with the keyword 'graphene' (Web of Knowledge 2014). As of 2013, the time of writing this review, there are a range of graphene production methods (as briefly discussed above), each of which carry their respective benefits, whilst at the same time producing different types of graphene (monolayer, multi-layer, *etc.*) which have different applications depending on the properties exhibited by each type of graphene. Fig. 4 depicts the application of graphene as a function of resistivity of the graphene, where it is seen that there are a range

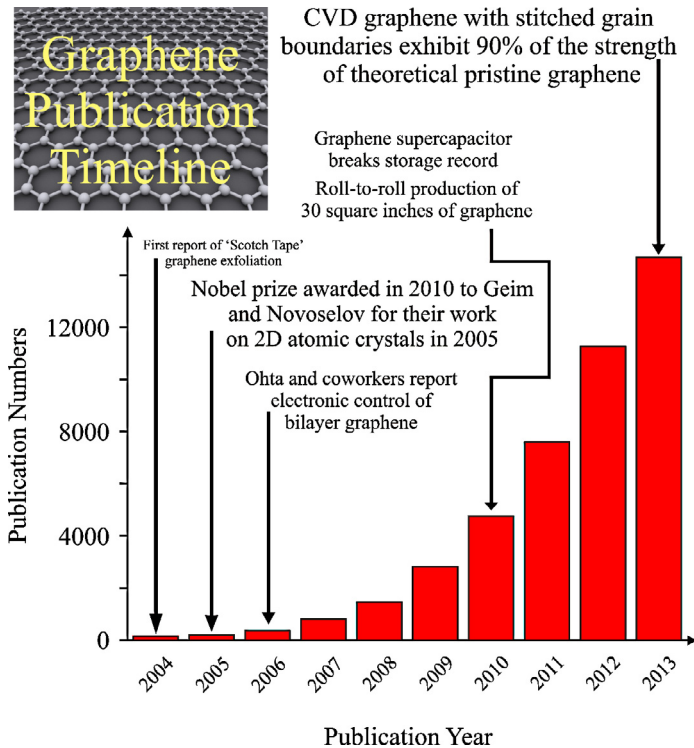


FIGURE 3

A short post-2004 graphene timeline representing the number of graphene-related academic publications (Source: Web of Knowledge, 08/02/14) and some pertinent graphene breakthroughs. Information acquired from Refs. [23,36,42,67,87,88].

of different technologies which could potentially be created utilizing the range of resistivities [53]. We continue from this section to discuss some of the many real-world benefits of graphene research.

High-speed electronics

One of the first proposed real-world applications of graphene is related to the conductivity of graphene being extremely high. One would think that a high conductivity would be ideal for high-speed electronics. While this is true, electronic devices consist of semiconductors which exhibit small yet significant band gaps which are required for 'on and off' states in an electronic device. Graphene however is a zero band gap material and hence has yet to make its commercial debut in this manner. Still, although scientists have worked tirelessly to create a graphene derivative with a band gap [54–56], the efforts have proved ineffective in terms of application, though recent work has elucidated the origin of the lack of a band gap in bilayer graphene lies with the twisting of the graphene sheet [57]. In fact, a twist as much of 0.1° is thought to collapse the band gap. Regardless of this, ultra-thin graphene transistors have been developed; an example of which is shown in Fig. 5 [58]. One particular problem with graphene based transistors originates from defects emerging upon the graphene sheet during the fabrication process of the device. That said, a literature report from 2010 emerged which utilized a self-aligning $\text{Co}_2\text{Si}-\text{Al}_2\text{O}_3$ nanowire as a gate in the graphene transistor which according to their work prevented device degradation and exhibited operational frequencies of 100–300 GHz [59]. This epitomizes

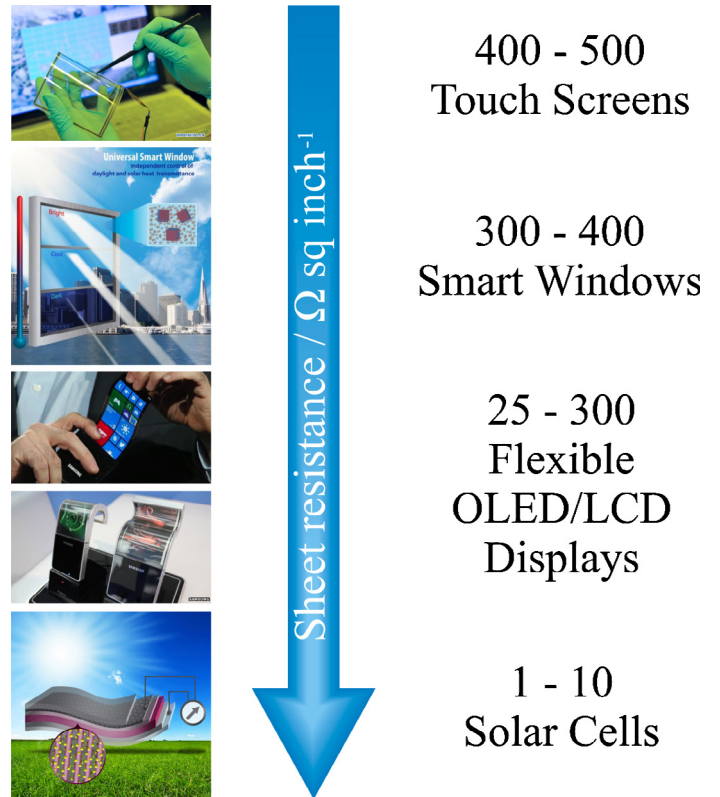


FIGURE 4

Potential applications graphene has to offer, depending upon the resistivity of the type of graphene. Adapted from Ref. [53] with permission from IOPScience.

how fast the graphene field is advancing and as a result it would be no surprise to see high-speed graphene transistors appear in consumer electronics within the next decade; a view which is shared by Novoselov et al. in their popular review [9].

Data storage

Reducing the size of data storage devices, or increasing the capacity of data storage devices whilst maintaining the size of a (flash-drive scale) piece of hardware is an area which is lesser studied in the graphene world, yet has seen some impressive discoveries. Researchers investigating the storage properties of graphene oxides have shown that indium tin oxide electrodes modified with polymers and graphene oxide exhibit the write-read-erase-read-rewrite cycle for a non-volatile memory device (Fig. 6) [60].

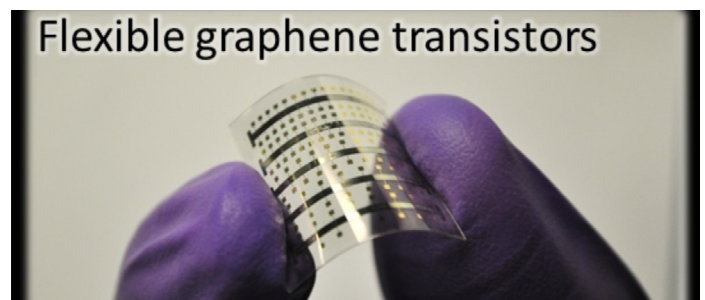


FIGURE 5

Ultra-thin flexible graphene transistor. Image reproduced from Ref. [58] with permission from IOPScience.

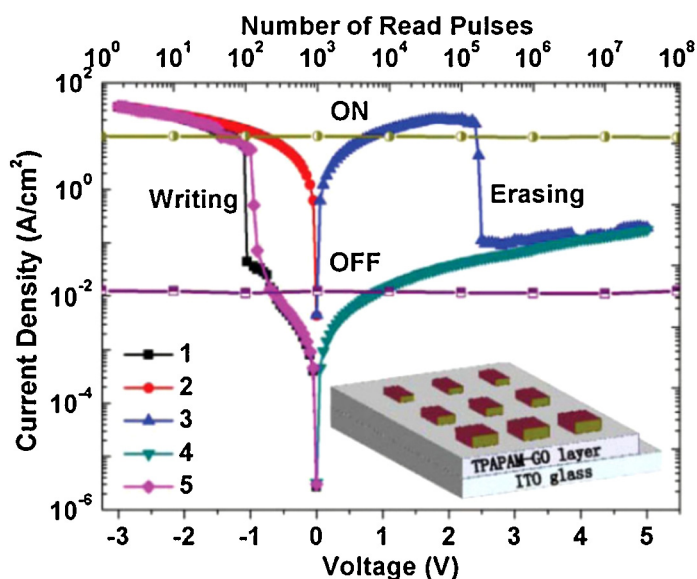


FIGURE 6

Current/voltage curves typical of the indium tin oxide electrode modified with polymers and graphene oxide discussed in Ref. [60]. The curves 1–5 represent the relevant stage in the write-read-erase-read-rewrite cycle. Reproduced from Ref. [60] with permission from Wiley.

Subsequent graphene oxide-based devices have emerged which exhibit data capacities of $0.2 \text{ Tbits cm}^{-3}$, which put into perspective is the equivalent of approximately *ten times* the storage of current readily available 16 GB USB flash drives [49]. With the ever growing need for increased data storage, graphene could in theory replace current solid state technologies in the future if research is tailored towards improving storage capacity. We argue that reducing the size of devices is not as much of an issue, considering USB flash drives are already small; however perhaps it would not be too long until a terabyte can be stored on a USB flash drive sized device whilst keeping the cost of the device to a minimum. More examples are presented in Refs. [61–63].

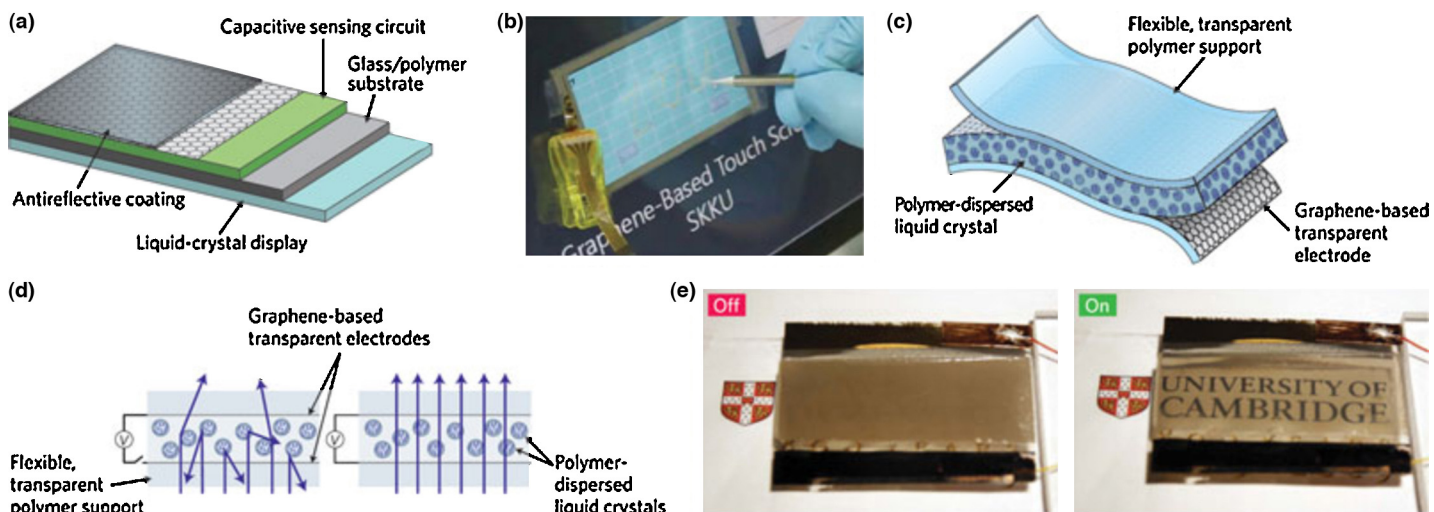


FIGURE 7

Schematic representing the production and design of an LCD Smart Window (a–d); and an actual LCD Smart Window in operation (e). Reprinted from Ref. [89] with permission from Nature.

LCD smart windows and OLED displays

Fig. 7 depicts a Liquid Crystal Display (LCD) Smart Window, a flexible device which is opaque until subjected to an electric field when it becomes transparent. The technology utilized in this device consists of a layer of liquid crystals sandwiched between two flexible electrodes consisting of a flexible polymer and graphene [64]; the electric field aligns the light-scattering liquid crystals to reveal a transparent background with a decal embedded in the middle. Organic light emitting diode (OLED) displays are also a massively researched area with work focused on using graphene as a flexible OLED counter electrode. Current OLED technologies utilize indium tin oxide counter electrodes which are brittle and in short supply in the world [65]; graphene on the other hand should be effectively limitless and flexible. Such devices are speculated to be the ones which sees graphene's commercial debut with reported interest from multinational businesses such as Samsung (see press release [66]). The applications of such technology include flexible touch screens for mobile and tablet devices. Perhaps with more research in this area it will not be too long until mobile phones have curved screens! There is even scope for flexible three-dimensional displays, which would have been unthinkable a decade ago.

Supercapacitors

Energy storage devices are utilized in almost every electronic device as they are responsible for delivering high electric currents over a short space of time. Supercapacitors are energy storage devices which deliver far higher currents than a normal capacitor. Most supercapacitor technologies utilize high internal surface area materials to store charge, and given that graphene exhibits an internal surface area of $2630 \text{ m}^2 \text{ g}^{-1}$ it seems an obvious choice. The capacitive storage record was broken by a graphene supercapacitor in 2010 in a report by Liu et al. [67]. One example of the need for a supercapacitor is to power electric cars which require high currents for acceleration. Several attempts of producing graphene-based supercapacitors are presented within the scientific ether; readers are referred to Refs. [68–73] for recent examples of

attempts to create such technologies. However, to date, these technologies are not yet widely available. Such graphene based supercapacitors are an exciting prospect as they could contribute to green energy solutions by use in electronic cars, trains and perhaps even one day, aeroplanes. Indeed, supercapacitors are already used in aeroplanes (such as the Airbus A380) but for minor electronic jobs such as opening fuselage doors.

Solar cells

Photovoltaic cells, or solar cells, are another potential application of graphene. Current solar cell technologies contain platinum based electrodes which carries at least two problems: the abundance of platinum on earth one would think is too low to create a planet's worth of solar cells, which is related to the second drawback - the cost. With graphene being an excellent conductor there is potential for graphene electrode design which would reduce cost and weight whilst maintaining efficiency, as described by Wang et al. [74]. Their graphene electrode in a dye-sensitized solar cell actually exhibited an efficiency of 7.8% which is 0.2% less than a platinum-based counter electrode, but produced at a fraction of the cost. Clearly it would be better to improve efficiency, but cutting the cost is as much an issue as improving efficiency for modern day technology. Nevertheless, any contribution to green energy will undoubtedly win over governments, activist groups, and home owners who feel they pay too much for their utility bills. Graphene solar cells, out of all the applications discussed here, are perhaps the furthest away from completion; however, solar cell research in general has been a slow process for many years, although any sign of progress is still progress nevertheless. Graphene has just given the field the 'shot in the arm' that it needed. Other works are provided in refs [75–79].

Electrochemical sensing

A vastly considered area for graphene application is the field of electroanalysis. After the graphene revolution a surge of reports emerged reporting graphene as a beneficial electrode material which catalyzed electrochemical reactions (see Refs. [10,80,81] for examples of graphene-attributed electrocatalysis). However it was proven that surfactants utilized in many liquid-phased based industrial graphene production processes were the source of observed electrocatalysis for several target analytes [82,83]. If one considers the structure of graphene, it is intuitive that the majority of the structure has a sparse electron density as the majority of the structure is effectively a basal plane of graphite which exhibits slow electron transfer rate kinetics. Fig. 8 summarizes the relative electrochemical reactivities of n -layered pristine graphene which shows that a single layer of graphene ($n = 1$) exhibits a slow electrochemical process, which improves as n approaches 8+ which becomes akin to that of graphite [10]. Though there is much discussion, many electrochemists believe that graphene itself, if orientated in a manner where the basal planes are exposed to the target analyte, does not catalyze electrochemical reactions [84]. However graphene does exhibit adsorptive properties in addition to the previously mentioned high conductivity which are exploited by many researchers where graphene is used as an anchor for electrode composite materials. One particular example worthy of note utilizes graphene as a support for DNA oligonucleotides typical of Alzheimer's disease [85]. These

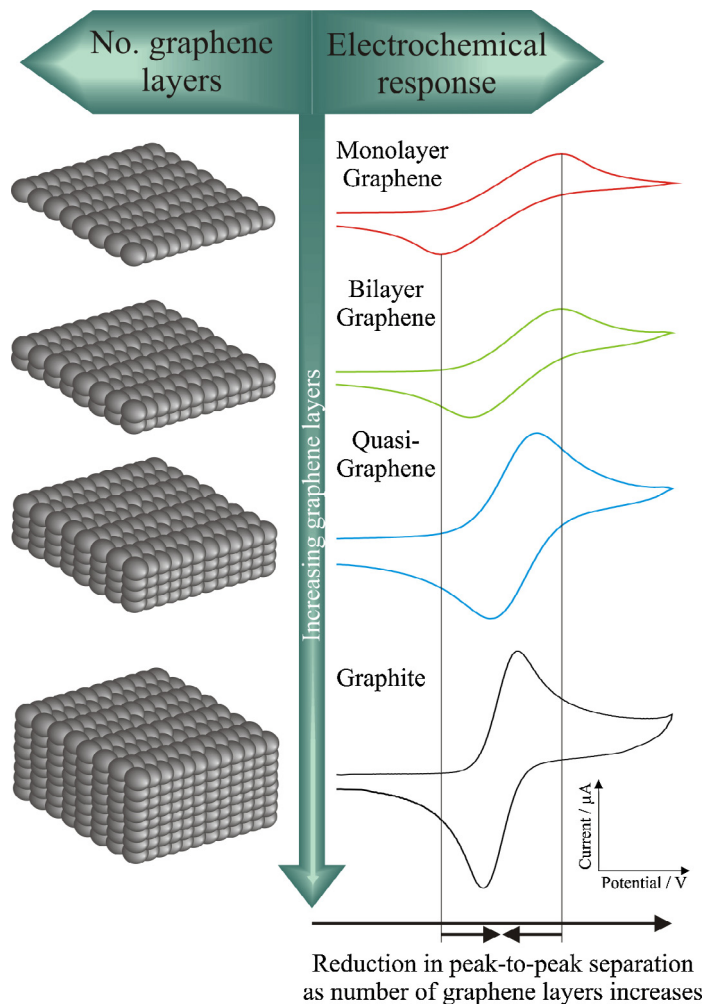


FIGURE 8

Schematic diagram depicting the relative electrochemical reactivities of n -layered pristine graphene towards a typical redox probe such as hexammine-ruthenium(III) chloride. The peak-to-peak separation in the voltammetric waves decreases as the number of graphene layers increases, indicating an increase in the heterogeneous electron transfer rate and thus better electrochemical performance. Figure developed from ideas reported in Ref. [90]. Note that this will change if defects (holes, dangling bonds, etc.) are introduced into the pristine graphene.

oligonucleotides specifically bind to the complimentary DNA strands associated with Alzheimer's disease which blocks the electrode surface. Then, changes in the impedance are measured which elucidate whether the Alzheimer's disease DNA is present in a sample. Such elegant work has potential for screening of not just Alzheimer's disease, but a whole host of different diseases (it is the author's belief that graphene-based technologies could be designed for point-of-care screening of sexually transmitted diseases, effectively reducing waiting times for patients). Furthermore, if the technology utilizes DNA strands specific to a particular disease, it would not be too presumptuous to think that perhaps many more diseases could be detected utilizing such technology. In addition, defect-rich graphenes can be engineered, creating reactive edge-planes/defects across the graphene surface with oxygenated functionalities (alkoxy, C–O) which will improve the electrochemical reactivity of graphene and thus have been

utilized by many for graphene research and is the key towards producing next-generation graphene based electrochemical derived sensors.

Concluding remarks

In the introduction we posed a few questions regarding whether or not graphene should be attracting the substantial funding it is receiving. The basis of such questioning we believe to be just, considering that carbon nanotubes (a sister material of graphene) have not yielded many significant improvements in commercial technologies since their discovery more than two decades ago. However, there has been far more attention turned to graphene than carbon nanotubes; this is because the properties of graphene are unrivalled, and thus it has captured the imagination of scientists all over the world, working tirelessly to create graphene-based electronic devices. We have presented a host of applications (and there are many others) with some even having primitive technologies available for demonstration, and with the demand for faster electronics, battery powered cars, point-of-care screening technology and more efficient energy generation increasing by the day, the world has good reason to get excited by the promise of graphene to replace silicon as *the* material at the cornerstone of all consumer electronics. Obviously the job is far from complete but with the amount of interest in graphene (compared to carbon nanotubes for instance), it would not be surprising if the first graphene-based commercially available technologies arrive within the next decade. The obstacles which need to be overcome are things such as mass production and graphene quality. For example, for many of the applications discussed to thrive they require large area, defect-free, grain boundary-free, monocrystalline graphene to be readily available and unfortunately, to date that has not been achieved. Other challenges are improving solar cell efficiency, tailoring graphene-based supercapacitors to exploit the massive specific surface area of graphene, and creating handheld platforms for electrochemical sensing *via* screen-printed (and related) graphene technology. We leave it to the reader to decide for themselves whether governments should be funding graphene research.

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