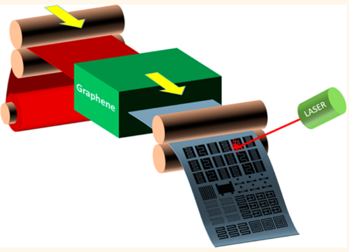
Direct Laser Writing of Graphene Electronics

Maher F. El-Kady[†,‡] **and Richard B. Kaner**[*,†,§]

[†]Department of Chemistry and Biochemistry and California NanoSystems Institute, University of California, Los Angeles, California 90095, United States, [‡]Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt, and [§]Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States

ABSTRACT One of the fundamental issues with graphene for logic applications is its lack of a band gap. In this issue of *ACS Nano*, Shim and colleagues introduce an effective approach for modulating the current flow in graphene by forming p—n junctions using lasers. The findings could lead to a new route for controlling the electronic properties of graphene-based devices. We highlight recent progress in the direct laser synthesis and patterning of graphene for numerous applications. We also discuss the challenges and opportunities in translating this remarkable progress toward the direct laser writing of graphene electronics at large scales.



Ever since graphene was first produced in the lab in 2004, it continues to fascinate researchers around the world with its potential for next-generation electronics. Graphene conducts electricity and heat better than anything else and has a combination of unique optical and mechanical properties. Electrons have mobilities in graphene over a hundred times those in silicon, the most widely used material in today's electronics. A fundamental issue was revealed in 2005 when Andre Geim's and Philip Kim's groups independently discovered that, unlike silicon, graphene has no band gap.[1] This means that electronic switches made out of graphene are always in a conductive state. Current can be made to move back and forth, but it cannot be turned on and off, meaning that there is no easy way to represent information storage bits.

Opening a Band Gap in Graphene. Researchers have shown that, by opening a band gap in graphene, it is possible to control the current flow in graphene switches. Opening a band gap in graphene has been achieved in several ways: by doping graphene, by confining electrons within graphene nanoribbons, by making a graphene nanomesh, by using an electric field between bilayered graphene, and even by bending graphene into nanogrooves.[2] While these approaches do create a band gap, this comes at the cost of lower electron mobility. Besides, these techniques still have issues for large-scale manufacturing to compete with current technology.

Creating p—n Junctions in Graphene. An alternative means of controlling current flow in graphene is by forming p—n junctions. Junctions can be realized by turning some regions of graphene into n-type and others into p-type semiconductors. The interfaces between the two regions are called p—n junctions and are the basic building blocks of most semiconductor electronic devices including transistors, diodes, solar cells, and light-emitting diodes. They are considered to be the active sites where the electronic action of the device takes place. This behavior is due to the depletion region of the p—n junction that enables the flow of electrons in one direction but not the other. Hence, the ability to form p—n junctions combined with precise control of the doping profiles in graphene is a necessary step to develop graphene electronics.

The carrier type in graphene and density can be controlled by using the electric field effect known as doping *via* local gates. This is achieved *via* complex patterning of graphene sheets into nanostructures and the local gating of the latter. Another approach involves doping graphene with atomic impurities, similar to those used in silicon-based technology. Simply doping with an acceptor (*e.g.*, boron) or a donor (*e.g.*, nitrogen) turns graphene into a p- or n-type semiconductor, respectively. Studies have shown that doping can be induced by the

* Address correspondence to kaner@chem.ucla.edu.

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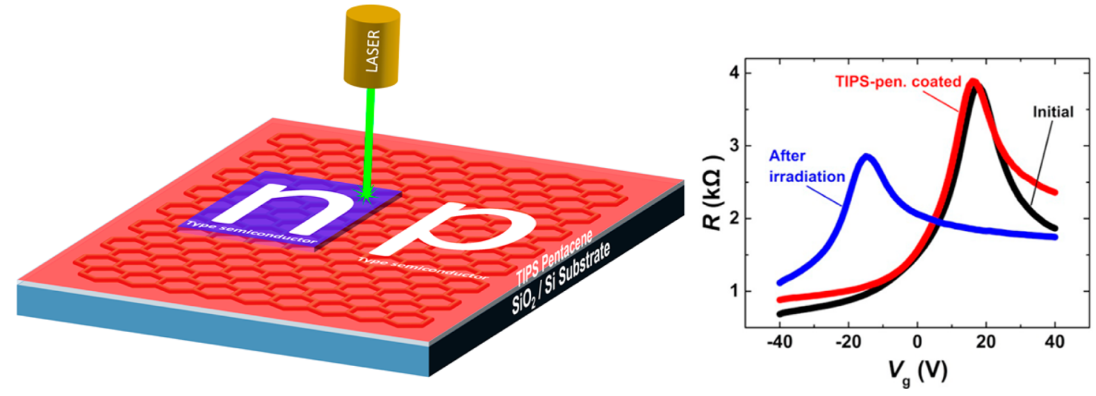

Figure 1. Direct laser writing of n-doped regions in graphene. (Left) Schematic illustration of writing n-doped regions in initially p-doped graphene. A variety of patterns can be etched onto the 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene)-coated graphene; shown here is a square pattern. (Right) Field effect transistor curves for graphene as fabricated (black line), after coating with TIPS-pentacene (red line), and after laser irradiation of the entire channel area (blue line).

interaction of graphene with the underlying substrate and/or surrounding atoms/molecules/nanoparticles. Most of these methods though require cumbersome lithographic fabrication techniques under an inert atmosphere and the application of an external voltage and, therefore, additional power consumption.

Direct Laser Writing of p−n Junctions. In this issue of *ACS Nano*, the Shim research group demonstrates a new approach for doping graphene in air using a simple laser writing technique.[3] Not only does this technique enable the effective control of carrier type and density in graphene, but it also can be used to dope graphene in patterns of any arbitrary shape.

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The laser-induced oxidation of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) spin-cast on top of an initially p-doped graphene causes charge transfer resulting in air-stable n-doping (Figure 1). By increasing the laser exposure time, the researchers found that the Dirac point of a graphene field effect transistor gradually shifts from positive (p-type) to zero (intrinsic) then to negative (n-type) gate voltages. These measured changes indicate that the degree of doping can be controlled by the duration of laser exposure and/or its intensity.

An interesting feature of this approach is that it only requires spin-coating of TIPS-pentacene and a low-power visible laser system. This facile and inexpensive strategy opens the door for fabricating cost-effective graphene electronics at large scales.

OUTLOOK AND FUTURE CHALLENGES

Despite the recent progress being made in graphene research, scalable integration of graphene into practical circuits remains challenging. Researchers need to address the integration problems associated with graphene in order to advance graphene electronics from the laboratory to the commercial scale. Another challenge involves the production of high-quality graphene at acceptable costs.

Direct Laser Writing of Graphene Electronics. Direct laser writing (DLW) has emerged as a promising technique for the rapid, inexpensive, and flexible fabrication of graphene for various applications. With this technique, it is possible to add, to remove, and to modify graphene without any physical contact between it and the tool. This single-step fabrication technique obviates the need for time-consuming and labor-intensive lithography. No photomasks, postprocessing, or complex clean room operations are required. Simple DLW systems have already been used for the direct synthesis, patterning, and transfer of graphene and for the direct writing of numerous graphene-based electronic devices (Figure 2). Examples include the direct writing of transistors, photodetectors, advanced supercapacitors and micro-supercapacitors, sensors, flexible circuitry, heat sinks, neural regeneration networks, and many other applications.

Furthermore, simple laser systems can be used for the direct writing of electronic devices. For example, using a consumer grade LightScribe DVD burner, our research group has developed an approach for the direct synthesis and patterning of graphene on a DVD disc.[5−7] Circuits and complex designs are directly patterned onto graphite oxide films coated on a substrate of choice. This technique shows promise for the mass production of graphene-based electronics. For example, we have produced over a 100 micro-supercapacitors on a single disc in less than 30 min.[6] This approach was also used by other

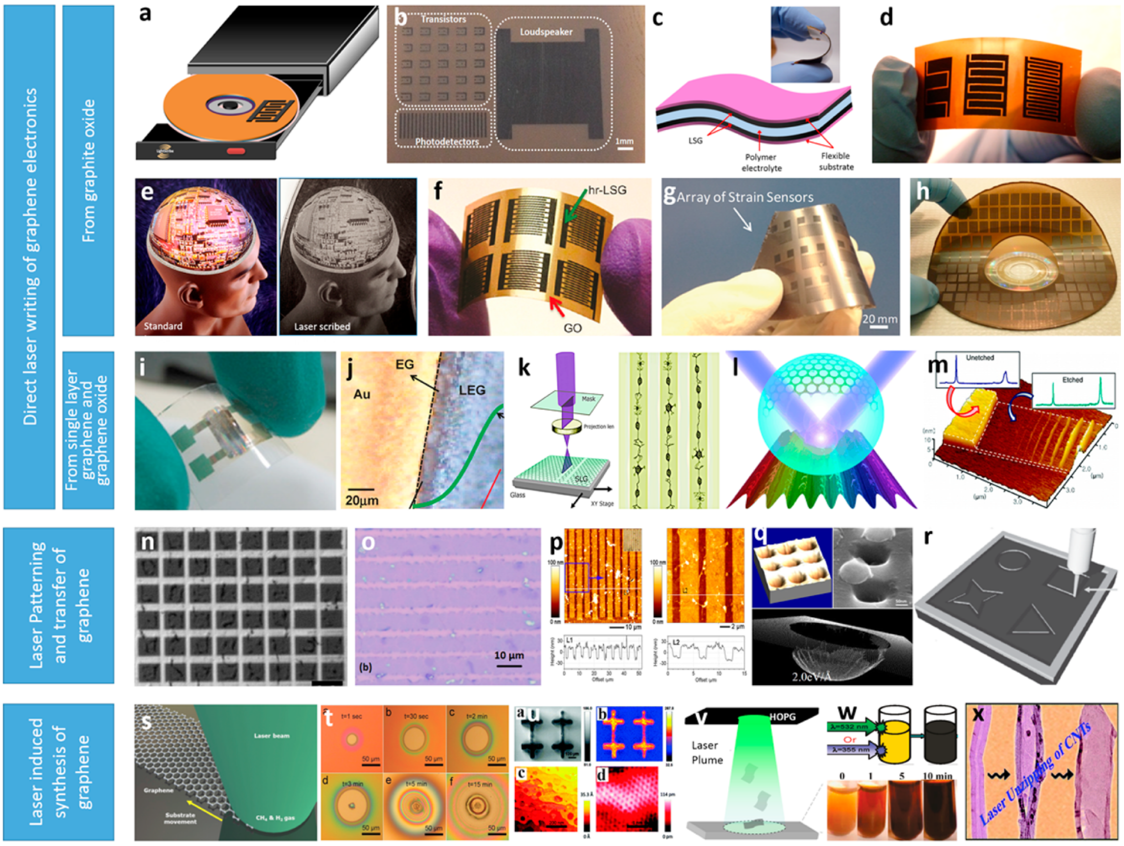

Figure 2. Direct laser writing of graphene electronics (a) Consumer grade LightScribe DVD burner can be used for the synthesis, patterning, and writing of graphene electronics from a graphite oxide precursor. This technique was used for the direct writing of (b) transistors, photodetectors, and loudspeakers. Reprinted with permission from ref 4. Copyright 2014 Nature Publishing Group. (c) Supercapacitors. Reprinted with permission from ref 5. Copyright 2012 American Association for the Advancement of Science. (d) Micro-supercapacitors. Reprinted with permission from ref 6. Copyright 2013 Nature Publishing Group. (e) Complex patterning. Reprinted from ref 7. Copyright 2012 American Chemical Society. (f) Gas sensors. Reprinted from ref 7. Copyright 2012 American Chemical Society. (g) Strain sensors. Reprinted with permission from ref 8. Copyright 2014 The Royal Society of Chemistry. (h) These electronic devices can be integrated on the wafer scale. Reprinted with permission from ref 6. Copyright 2013 Nature Publishing Group. Furthermore, pristine single-layer graphene can be manipulated by lasers for the direct writing of (i) humidity sensors. Reprinted with permission from ref 9. Copyright 2012 Elsevier. (j) Schottky junction photodetectors. Reprinted from ref 10. Copyright 2011 American Chemical Society. (k) Interfacing graphene with neurons could stimulate their electrical properties for neural regeneration. Reprinted with permission from ref 11. Copyright 2013 Nature Publishing Group. (l) Superhydrophobic surfaces. Reprinted with permission from ref 12. Copyright 2012 Wiley-VCH Verlag. (m) Heat sink. Reprinted from ref 13. Copyright 2011 American Chemical Society. Lasers can also be used for the patterning and transfer of graphene: (n−r) examples of patterning graphene from the micro- to the nanoscale. (n) Reprinted with permission from ref 14. Copyright 2011 IOP Publishing Ltd. (o) Reprinted with permission from ref 15. Copyright 2014 AIP Publishing. (p) Reprinted with permission from ref 16. Copyright 2010 Elsevier. (q) Reprinted with permission from ref 17. Copyright 2011 IOP Publishing. (r) Reprinted with permission from ref 18. Copyright 2012 Wiley-VCH Verlag. Lasers can be used for the direct synthesis of graphene using (s) chemical vapor deposition (CVD) from CH_4 and H_2. Reprinted with permission from ref 19. Copyright 2011 American Institute of Physics. (t) From the solid polymer PMMA. Reprinted with permission from ref 20. Copyright 2012 American Institute of Physics. (u) Epitaxial growth from SiC. Reprinted from ref 21. Copyright 2010 American Chemical Society. (v) Pulsed laser deposition from HOPG. Reprinted with permission from ref 22. Copyright 2011 American Institute of Physics. (w) Deoxygenation of a colloidal dispersion of graphite oxide. Reprinted from ref 23. Copyright 2010 American Chemical Society. (x) Unzipping of carbon nanotubes. Reprinted with permission from ref 24. Copyright 2011 Royal Society of Chemistry.

research groups for the direct writing of sensing, electronic, optoelectronic, and electroacoustic graphene-based devices.[4,8] Given that lasers have been widely adapted in industry for metal cutting and welding, and that lasers are available in a wide range of wavelengths and power, laser processing of graphene holds promise for commercial applications.

Roll-to-Roll Processing of Graphene Electronics. Unlike conventional silicon, graphene can be used to make flexible and stretchable electronics, whereas, if you try to bend a silicon wafer, it will shatter into pieces. Graphene may thus open new technological markets that cannot be approached by conventional silicon electronics. For example, flexible graphene electronics could be integrated into a new generation of smart garments, flexible displays, toys, and animated posters. They could be embedded into smart bandages to monitor and to help the healing of wounds or into RFID tags that can be used for tracking products.

Researchers need to explore ways to make and to integrate graphene

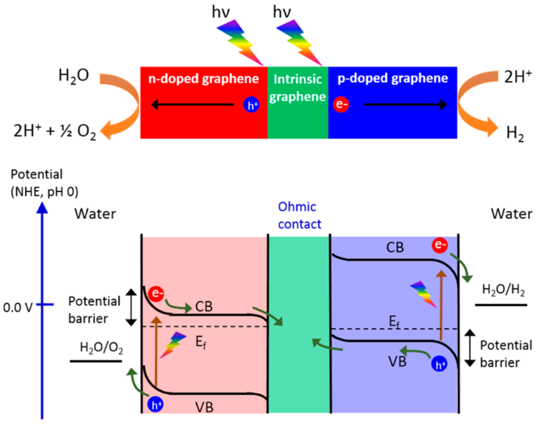

Figure 3. Laser engineering of an efficient graphene photocatalyst for direct water splitting. The doping level of graphene can be controlled to produce an n-type/intrinsic/p-type interface device. This structure enables efficient creation and separation of electron–hole pairs due to the built-in voltage across the graphene/water interface. This results in the efficient reduction of water to H_2 at the p-type domains and oxidation to O_2 at the n-type domains.

into electronics using scalable methods such as roll-to-roll processing. Here, some notable progress has been made for the roll-to-roll synthesis of graphene. For example, in 2010, the Iijima group made 30 in. single-layer graphene films for transparent electrodes using chemical vapor deposition.[25] Three years later, researchers at Sony Corp. pushed this size to reach 100 m long graphene films.[26] The next step should focus on the direct integration of the produced graphene films into useful electronic devices, as illustrated in the table of contents image. Given its simplicity and low cost, DLW opens the door for the realization of this goal. If successful, graphene devices fabricated with this process could be available at a fraction of the cost of traditional semiconductor manufacturing methods.

> Researchers need to explore ways to make and to integrate graphene into electronics using scalable methods such as roll-to-roll processing.

Photocatalytic Applications. Shim and co-workers observed that graphene enhances the photo-oxidation of TIPS-pentacene, an important feature that might enable the use of graphene in efficient photocatalytic systems. Of scientific and technological interest is the production of hydrogen from photocatalytic water splitting by directly utilizing the energy from sunlight. Extensive efforts have been made to develop efficient heterogeneous photocatalysts by investigating new semiconductor materials. However, most of these photocatalysts are either unstable due to photocorrosion or work only under UV light due to their large band gaps. Graphene is considered to be an ideal candidate for photocatalysis due to its high surface area, transparency, and superior electron and hole mobility.[27] The ability to pattern graphene p–n junctions of arbitrary shapes could enable an interesting approach for the design of a new generation of highly efficient and stable diode photocatalysts.[28,29] Figure 3 shows a suggested device: p-doped graphene/intrinsic graphene/n-doped graphene. The built-in potential within this p–n diode with ohmic contacts promotes the rapid dissociation and transport of the photoexcited electron–hole pairs, which, in turn, could improve catalytic efficiency. Oxidation and reduction cocatalysts can also be added to increase the efficiency of the process. This device architecture could provide understanding of the mechanism of direct water splitting.

Tremendous progress in graphene research has been made during the past decade. However, the translation of this progress into marketable products could be accelerated through partnerships between academia and industry. For example, the University of Cambridge announced a few days ago that collaboration between its graphene research center and the company Plastic Logic resulted in a successful demonstration of the first flexible display incorporating graphene in its pixels' electronics.[30] This work may enable the realization of a new generation of flexible and perhaps foldable electronics. Another example is the Vorbeck Materials Corp. demonstration of printing graphene circuits and other electronic components on paper using gravure and flexographic printing in a manner similar to printing newspapers, thus promising low cost. Vorbeck's proprietary graphene material was developed in the research laboratories of Princeton University.[31] A few months ago, Vorbeck released the first graphene-based flexible battery that can be attached to any existing bag strap to enable portable charging-on-the-go.[31] Clearly, the future of graphene for electronics is promising, and it may not be too long before we see personal graphene-based products.

Conflict of Interest: The authors declare no competing financial interest.

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