

Laser-Induced Graphene

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CONSPECTUS: Research on graphene abounds, from fundamental science to device applications. In pursuit of complementary morphologies, formation of graphene foams is often preferred over the native two-dimensional (2D) forms due to the higher available area. Graphene foams have been successfully prepared by several routes including chemical vapor deposition (CVD) methods and by wet-chemical approaches. For these methods, one often needs either high temperature furnaces and highly pure gases or large amounts of strong acids and oxidants. In 2014, using a commercial laser



scribing system as found in most machine shops, a direct lasing of polyimide (PI) plastic films in the air converted the PI into 3D porous graphene, a material termed laser-induced graphene (LIG). This is a one-step method without the need for hightemperature reaction conditions, solvent, or subsequent treatments, and it affords graphene with many five-and sevenmembered rings. With such an atomic arrangement, one might call LIG "kinetic graphene" since there is no annealing in the process that causes the rearrangement to the preferred all-six-membered-ring form. In this Account, we will first introduce the approaches that have been developed for making LIG and to control the morphology as either porous sheets or fibrils, and to control porosity, composition, and surface properties. The surfaces can be varied from being either superhydrophilic with a 0° contact angle with water to being superhydrophobic having >150° contact angle with water. While it was initially thought that the LIG process could only be performed on PI, it was later shown that a host of other polymeric substrates, nonpolymers, metal/plastic composites, and biodegradable and naturally occurring materials and foods could be used as platforms for generating LIG. Methods of preparation include roll-to-roll production for fabrication of in-plane electronics and two different 3D printing (additive manufacturing) routes to specific shapes of LIG monoliths using both laminated object manufacturing and powder bed fabrication methods. Use of the LIG in devices is performed very simply. This is showcased with high performance supercapacitors, fuel cell materials for oxygen reduction reactions, water splitting for both hydrogen and oxygen evolution reactions coming from the same plastic sheet, sensor devices, oil/water purification platforms, and finally applications in both passive and active biofilm inhibitors. So the ease of formation of LIG, its simple scale-up, and its utility for a range of applications highlights the easy transition of this substrate-bound graphene foam into commercial device platforms.

1. INTRODUCTION

Recent research on graphene has led to its successful use in applications ranging from electronics to catalysis by taking advantage of the excellent chemical and physical properties of graphene.^{1–3} In many applications, graphene is engineered into three-dimensional (3D) porous structures to provide high surface area yet maintain its high mobility and mechanical stability.^{4–7} Conventional methods for the fabrication of 3D graphene structures include the assembly of graphene oxide (GO) into a foam. However, this approach suffers from the need for the GO precursor to be prepared through its oxidative acid synthesis route.^{4,5} Chemical vapor deposition (CVD) on porous substrates also produces 3D graphene, but the high temperature conditions and subsequent etching and drying process may hinder its scalable production.^{6,7}

Recently, we developed a facile and scalable approach to the formation and patterning of 3D porous graphene on polyimide (PI) under ambient conditions by using a commercial CO_2 infrared laser scriber, which is a common tool often found in machine shops.⁸ This one-step process to make laser-induced

graphene (LIG) could therefore be an advantage over conventional methods for the synthesis of 3D graphene. In comparison to the laser-reduced graphene method, which uses lasers to reduce GO films to graphene, the avoidance of using GO precursors greatly simplifies the process and reduces the cost.⁹ In this Account, we begin with the synthesis of LIG from PI and the development of this technique for tuning its morphology and composition, and then the conversion of naturally occurring materials to LIG. We further discuss two routes for the large scale production of LIG: a roll-to-roll method for fabrication of in-plane electronics and 3D printed LIG on the macroscopic scale. Then, we will introduce various applications for LIG that range from use in renewable energy devices to water treatment platforms.

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Figure 1. LIG formation under ambient conditions. (a) Schematic of the synthesis process of LIG from PI. (b) SEM image of LIG patterned into an owl shape at an image density of 1000 PPI; scale bar is 1 mm. (c) SEM image of the LIG film circled in (b); scale bar is 10 μ m. Upper right inset is the corresponding higher magnification SEM image; scale bar is 1 μ m. Lower left inset is the schematic for 1000 PPI illustrating the overlapping of spots by the laser pulses. (d) HRTEM image of LIG; scale bar is 5 nm. Average lattice space of ~3.4 Å corresponds to the (002) planes of graphitic materials. (e) Cs-correction STEM image taken at the edge of a LIG flake; scale bar, 2 nm. (f) TEM image of selected area indicated as a rectangle in (e). Panels (a)–(f) are adapted with permission from ref 8. Copyright 2014 Springer Nature: *Nat. Commun.* (g) LIGF patterned in the shape of an R letter; scale bar is 1 mm. (h) LIGF with thickness of ~1 mm made at an image density of 500 PPI; scale bar is 500 μ m. Inset is the schematic 500 PPI. (i) SEM of LIGF (boxed in h) at higher magnification; scale bar is 2 μ m. Panels (g)–(i) and the inset in (c) are adapted with permission from ref 11. Copyright 2018 Elsevier.

2. FORMATION OF 3D HIERARCHICAL LIG

In this section, we introduce the synthesis and property engineering of LIG, and then discuss the extension to LIG formation on more common substrates.

2.1. LIG Formation on PI under Ambient Conditions

The transformation of PI to LIG is a photothermal process that is associated with the localized high temperature and pressure produced by laser irradiation (Figure 1a–c).^{8,10} The hierarchical structure and the presence of abundant wrinkles on the graphene surface (Figure 1d) produce a surface area of \sim 340 m²/g, which is comparable to that of the wet-chemistryderived 3D graphene.^{5,8} The aberration-corrected scanning transmission electron microscopy (Cs-STEM) images (Figure 1e-f) reveal an unusual polycrystalline feature of LIG. Instead of the conventional hexagon lattice, the carbon of LIG exists in a hexagon and pentagon-heptagon hybrid lattice (Figure 1f). This could be termed "kinetic graphene" since there is no time for equilibration to the standard hexagon lattice due to the rapid cooling following laser irradiation.

The lasing parameters have a profound effect in controlling the chemical and physical properties of LIG.^{8,11} In general, amplifying the laser power can increase the LIG thickness while improving the conductivity. LIG reaches its highest crystallinity at a laser power of 4.8 W with fewest defects and a maximum graphene domain size. In terms of laser fluence needed to make LIG from PI, ~ 5.5 J/cm² is where LIG starts to form.^{8,11} The morphology of LIG can also be controlled by the image density, which is guided by the pulse width modulation or pulses per inch (PPI), and the lines per inch (LPI).¹¹ Inches are used since that is the common setting on the laser tool; 1 in. = 2.54 cm. At an image density of 1000 PPI × 1000 LPI and a ~ 100 μ m laser spot size, the LIG will adopt an in-plane porous structure (Figure 1c).^{8,11} As the image density decreases to 500 PPI × 500 LPI with a ~ 60 μ m laser spot size, the LIG starts to produce out-of-plane fibers (LIGF) and form a vertically aligned forest morphology (Figure 1g-i).¹¹

2.2. LIG Formation on Modified PI and Phenolic Resin

The modification of the graphene composition by heteroatom doping or formation of hybrid material presents an effective approach to engineer the properties and functions of nanomaterials.^{5,12,13} Conventional methods for tuning the composition of graphene include a CVD process that is performed at high temperature^{12,14} and a wet-chemistry process that includes a synthesis route such as to GO, nanoparticle deposition, and GO reduction.^{5,13} Direct lasing



Figure 2. In situ formation of LIG composite. (a) Schematic illustration for the formation of m-PI. Energy-dispersive X-ray spectroscopy of B-LIG for (b) boron, (c) carbon, and (d) oxygen. TEM images of LIG containing new uniformed sizes of (e, g) Co_3O_4 and (f, h) MOO_2 crystalline nanoparticles. The scale bars are 5 μ m in (b)–(d), 100 nm in (e) and (f), and 5 nm in (g) and (h). Adapted with permission from refs 15 and 16. Copyright 2015 American Chemical Society.

on modified PI (m-PI) under ambient conditions for in situ modification of graphene composition could therefore be an advantage. Figure 2a shows the scheme for the preparation of m-PI, which includes the mixing of poly(amic acid) (PAA) with additives in *N*-methyl-2-pyrrolidone, the evaporation of the *N*-methyl-2-pyrrolidone solvent, and the dehydration of PAA to form PI. The m-PI is then subjected to laser irradiation to afford LIG with varying compositions. For example, borondoped LIG (B-LIG) is formed when m-PI is prepared from PAA containing boric acid (Figure 2b-d). By changing the additive to metal complexes, hybrid LIG-based materials containing diverse metal oxide nanoparticles with uniform size distribution and high crystallinity can be prepared (Figure 2e-h).

Wu, Hu and co-workers produced LIG and metal-doped LIG from phenolic resin (PR) or metal salt doped PR, respectively, using a 405 nm semiconductor laser.¹⁷ Solutions of PR and the dopant were spin-coated onto substrates including polymers, glass, paper, copper, silicon and plant leaves. The LIG prepared from PR-Fe coated on poly(ethylene terephthalate) had the lowest sheet resistance. They confirmed that a CO_2 laser either produced no LIG from PR if the power was low, or completely ablated the PR if the power was too high.

2.3. LIG Formation on PI under Controlled Atmosphere

While the formation of LIG under ambient conditions provides a facile synthesis route,⁸ lasing under a controlled atmosphere has led to changes in surface morphology and chemical composition of the LIG, resulting in tunable hydrophobicity and hydrophilicity of the LIG surface.¹⁸ Figure 3a depicts the lasing scheme with a photograph of the apparatus shown in Figure 3b. The controlled atmosphere lasing method allows



Figure 3. LIG formation under controlled atmosphere. (a) Scheme and (b) photograph of the apparatus for the fabrication of LIG under a controlled atmosphere. Contact angles of LIG prepared in (c) ambient air, (d) air (chamber), (e) O_2 (chamber), (f) Ar (chamber), (g) H_2 (chamber), and (h) SF₆ (chamber). Adapted with permission from ref 18. Copyright 2017 WILEY-VCH.



Figure 4. LIG formation on wood. (a) Schematic illustration of wood-derived graphene via laser induction. (b) Photo of LIG patterned into a letter R on pinewood. (c) SEM image of P-LIG-70, where "P" stands for pinewood and 70 for the laser power setting of 70%. Inset shows the cross section. Scale bars in (c) and the inset are 500 μ m. (d) TEM of P-LIG-70 showing a graphene surface with wrinkles. Inset is the high-resolution TEM image. The scale bar is 20 nm in (d) and 4 nm in the inset. (e) Schematic illustration of lignocellulose structure in wood (Adapted with permission from ref 21. Copyright 2011 Elsevier). The tightly packed cellulose is embedded in a matrix of cross-linked hemicellulose and lignin. (f) Raman spectra of different woods lased at 70% laser power setting on the tool. B = birch, O = oak. Figure 4 is adapted with permission from ref 20. Copyright 2017 WILEY-VCH.

the formation of LIG under various gas environments such as O_2 , Ar and SF₆, which mimics the traditional CVD process for the growth and modification of graphene without the need of high-temperature oven heating.¹⁹ It is found that lasing on PI under ambient or an oxidizing atmosphere leads to a superhydrophilic surface (contact angle ~ 0°, Figure 3c–e), while a superhydrophobic surface (contact angle >150°) can be obtained when inert or reducing gas is applied (Figure 3f–g).¹⁸ The variation of superhydrophobicity is found to correlate with the LIG surface oxygen content and morphology.¹⁸ The decrease in oxygen content and the formation of carbon nanoparticles on the surface will both enhance the hydrophobicity. The superhydrophobicity can be further enhanced by in situ fluoro-doping when PI is lased in a chamber charged with SF₆ (Figure 3h).¹⁸

2.4. LIG Formation on Lignocellulose Materials

LIG has been successfully transformed from PI, yet the majority of other polymer substrates ablate when irradiated under ambient conditions.⁸ In a recent study, our group found that LIG can be formed on wood when it is lased under an inert or reducing atmosphere using a defocused laser spot (\sim 1 mm).²⁰ However, direct lasing in room atmosphere ablated or burned the wood. Figure 4a shows the scheme for the fabrication of LIG on wood. The LIG on top of the wood can be patterned into a computer-designed shape (Figure 4b). The resulting LIG is a 3D network with porosity controllable by laser power (Figure 4c).²⁰ The graphene contains abundant wrinkles and shows characteristic graphene fringes on the surface (Figure 4d). Mechanistic studies reveal that wood containing cross-linked lignocellulose with higher lignin



Figure 5. LIG formation on various substrates. Photos of LIG patterned on (a) a coconut, (b) a potato, (c) a piece of bread, (d) a cork, (e) paper, and (f) a muslin cloth. The scale bars are 1 cm. (g) LIG on muslin cloth wrapped around a marker. All owls depicted are 60 mm in height. Adapted with permission from ref 22. Copyright 2018 American Chemical Society.



Figure 6. Scheme for roll-to-roll production of LIG film. LIG is first formed on the PI sheet, and then developed in a catalyst bath to form hybrid materials.

content is more favorable for the synthesis of high-quality graphene (Figure 4e,f). 20

Inspired by the formation of LIG on wood, various lignocellulose materials from nature have also been successfully converted into LIG under ambient conditions (Figure 5), which permits the subsequent fabrication of biodegradable nanodevices.²² For materials with high lignin content (~90%), direct writing on the surface using a defocused CO_2 laser under ambient conditions leads to the formation of LIG, as shown in Figure 5a and b on coconut and potato, respectively.²² For materials with high cellulose content (>50%) such as paper and fabrics, pretreatment with a fire retardant is helpful to inhibit the ablation of materials in air and to facilitate the formation of LIG (Figure 5e and g).²²

3. SCALE-UP PRODUCTION OF LIG

While laser-assisted formation of LIG has been shown to be a potent materials manufacture technique, the viability of scaleup production is essential to meet the mass and volume demands in practical applications. In this section, two strategies are proposed for the mass production of LIG.

3.1. Roll-to-roll production of LIG film

The roll-to-roll production method is feasible for the consecutive synthesis of LIG film and the subsequent development of hybrid materials for different applications. A scheme for this method is depicted in Figure 6, which includes a LIG forming chamber and an optional catalyst electrodeposition bath. In contrast to laboratory design, here the CO_2 laser is static and the laser beam is focused to a line.⁸ The PI sheet is then fed continuously into the lasing chamber by a supply roll and the in-plane 3D LIG film will form on two-sided irradiation. After that, the LIG film can be immersed into a catalyst electrodeposition bath for the formation of hybrid materials. The film is then collected by a take-up roll after drying.

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3.2. 3D Printing of LIG

Although laser induction on PI sheet can produce 3D porous graphene, the LIG or LIGF are embedded in PI with thicknesses ranging from 20 μ m to 1 cm.^{8,20} In pursuit of thicker LIG coverage in certain applications, 3D printing of LIG on a macroscopic scale would be desirable. Current methods for the fabrication of macroscopic 3D graphene foam (GF) includes the growth of graphene on metallic foam and the subsequent removal of metal,^{6,7} and the assembly of GO by a hydrothermal reaction.^{4,5} However, these methods either require several fabrication steps or they can have poor control over the morphology of the printed objects. Taking advantage of the LIG process, two approaches for 3D printing of GF with fine structure have been developed; one is based on laser sintering of metal powder, and the other is based on laminated objected manufacturing (LOM).

Figure 7a shows the scheme for the laser sintering method using additive manufacturing.²³ Briefly, a 10.6 μ m laser is used



Figure 7. 3D printing LIG by laser-assisted sintering. (a) Schematic of in situ synthesis of 3D GF using a simulated 3D printing process. (b) Photographs of 3D printed GF before and after dissolving the Ni. Scale bars are 5 mm. Reproduced with permission from ref 23. Copyright 2017 American Chemical Society.

to heat the Ni/sucrose mixture, in which Ni acts as the catalyst to convert sucrose into graphene. The 3D structure is built by consecutive addition of Ni/sucrose layers and its subsequent laser-assisted conversion to Ni/graphene. After the etching of Ni and removal of solvent, a 3D printed GF is formed with high porosity (~99.3%), high conductivity (~8.7 S cm⁻¹), and remarkable storage modulus (~11 kPa).²³ In addition, the shape of the 3D GF is controlled by computer design (Figure 7b).

The second method for fabrication of 3D GF based on LOM is schematically illustrated in Figure 8.²⁴ In this approach, two PI sheets with embedded LIG are first adhered by ethylene glycol contact forces to form a sandwich structure (Step 2). The PI layer on top is then lased by using a 10.6 μ m fiber laser. A macroscopic GF can be prepared after repeating Step 2 and Step 3. The LIG generated by the 10.6 μ m has a resolution of ~75 μ m. In order to achieve higher GF resolution, a 1.06 μ m fiber laser with a theoretical 10× higher resolution was further employed to mill the bulk LIG (Figure 10b).²⁴ In this process, LIG is ablated at a fluence of 6 J/cm² to make geometries with finer resolution. Figure 8c,d demonstrates two examples of GF, a complex cube shape and a R letter, prepared by the LOM method.

4. APPLICATIONS OF LIG

Since its discovery, LIG has been intensively studied and developed for applications including microfluidic systems, electronic devices, catalysis systems, water purification systems and biosensor.^{19,20,25–29} Generally, there are three ways to explore its applications, which includes the direct use of pristine LIG, ^{8,25,27} the formation of LIG composite in situ,¹⁶ and the deposition of active materials ex situ.^{20,26,30} In this section, we will review the applications of LIG in the fields of renewable energy and water treatment.

4.1. Flexible Microsupercapacitor for Energy Storage

Two types of microsupercapacitors (MSC) have been developed from LIG by directly writing the interdigitated inplane electrodes on PI sheet: one is based on the double-layer capacitive behavior of graphene carbon (Figure 9a),^{8,15} and the other is based on the pseudocapacitive behavior of graphenebased hybrid materials (Figure 9b).²⁶ The areal capacitances of MSCs are summarized in Figure 9c. Due to the polycrystalline nature of graphene (Figure 1e,f) and the 3D network of highly conductive graphene with high surface area and abundant



Figure 8. 3D printing LIG by LOM method. (a) Scheme of the LOM process. (b) Scheme of the fiber laser milling process. Photographs of GF in (c) a complex cubic shape, and (d) a R letter. Reproduced with permission from ref 24. Copyright 2018 WILEY-VCH.



Figure 9. LIG-derived MSCs. (a) Schematic diagram for LIG-MSC device architecture. Adapted by permission from ref 8. Copyright 2014 Springer Nature. (b) Scheme of MSC with pseudocapacitive materials deposited atop the interdigitated LIG electrodes. (c) Comparison of the areal capacitance of LIG-derived MSCs with data from ref 38. (d) Ragone plots of LIG-MnO₂-2.Sh, LIG-PANI-15, and LIG-FeOOH//LIG-MnO₂ with literature refs 31–34. (e) Schematic illustration showing the fabrication process for assembling a single LIG-SC and stacked LIG-SC. Adapted with permission from ref 35. Copyright 2015 American Chemical Society. (f) Capacitance retention of LIG-MnO₂-2.Sh, LIG-PANI-15, and LIG-FeOOH//LIG-MnO₂ at different bending cycles with a $\alpha_{\rm B}$ of ~90°. Inset shows the definition of bending angle $\alpha_{\rm B}$. Panels (b)–(d) and (f) are adapted with permission from ref 26. Copyright 2016 WILEY-VCH.

wrinkles,⁸ the MSCs based on pristine or heteroatom-doped LIG structure exhibit capacitance of $4-16.5 \text{ mF/cm}^2$, a value that is comparable or higher than other carbon-based MSCs at the same current densities.^{8,29} The areal capacitance can be further improved by ex situ electrodeposition of pseudocapacitive materials (polyaniline (PANI), FeOOH and MnO₂) on

LIG.²⁶ For example, the areal capacitances of LIG-PANI and LIG-MnO₂ reach values of 360 and 930 mF/cm², respectively, 2 orders of magnitude higher than those of carbon-based capacitances.^{8,15,26} The Ragone plots show that these pseudocapacitive MSCs have high volumetric energy densities at high power densities, values that are among the best for

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Figure 10. Oxygen reduction catalytic performance of MO-LIG-A. (a) Cyclic voltammetry curves of LIG-A, 5Co-LIG-A, 5Fe-LIG-A, 5Mo-LIG-A, and Pt/C. Rotating-disk voltammograms of (b) 5Co-LIG-A, (c) 5Mo-LIG-A, and (d) 5Fe-LIG-A. Insets are corresponding Koutecky–Levich plots at different potentials. All data were collected in O_2 -saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹. Reproduced with permission from ref 16. Copyright 2015 American Chemical Society.



Figure 11. Overall water splitting electrode fabricated on LIG. (a) Scheme and (b) photograph for the overall water splitting electrodes made on two sides of PI sheet. (c) Photograph showing hydrogen and oxygen bubbling over the P-LIG-Co-P (left electrode) and P-LIG-NiFe (right electrode) surfaces powered by two 1.5 V batteries in series. (d) HER and OER windows (*iR* compensated) of pine-wood-derived LIG deposited with Co-P or NiFe in 1 M KOH aqueous solution. GC: glassy carbon electrode (CH Instrument). (e) HER and OER Tafel slopes derived from (d). (f) Durability test of wood-derived electrodes. Panels (a) and (b) are adapted with permission from ref 30. Copyright 2017 American Chemical Society. Panels (c)–(f) are adapted with permission from ref 20. Copyright 2017 WILEY-VCH.

reported available energy storage devices.^{31–34} The energy storage performance of MSCs can also be improved by physical engineering.³⁵ Figure 9e shows the scheme for the

assembly and analysis of a multilayered LIG-MSC.³⁵ In each PI film, both sides are converted into LIG and work as the capacitive materials. With this similar design principle, a 1000-

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Figure 12. LIG as membrane for water—oil separation. (a,b) Topview SEM image of LIG filter. (c) Water droplet on the surface of the LIG filter; the measured contact angle is 155° . (d–f) Filtration of CHCl₃/H₂O mixture with the LIG filter. (d) Water does not go through the filter; (e) CHCl₃ goes through the filter; (f) water stays on top of the filter even after all of the CHCl₃ went through. Reproduced with permission from ref 18. Copyright 2017 WILEY-VCH.

V SC was demonstrated by Li et al.³⁶ All the MSCs demonstrate excellent cyclability and mechanical flexibility, which affords it great potential in the use of wearable electronics.^{8,15,26,35} For examples, the capacitances are over

95% retained after 10000 bending cycles at a $\alpha_{\rm B}$ of ~90° (Figure 9f).²⁶

4.2. Oxygen Reduction Reaction Electrocatalysts

The in situ formation of metal oxide nanoparticles embedded in LIG can expand its use as the electrocatalysts for the oxygen reduction reaction (ORR).¹⁶ Pure LIG can only catalyze the reduction of oxygen by a 2.7 e^- process and at an O₂/OH⁻ half redox peak $(E_{1/2})$ of 0.66 V (Figure 10a). However, the formation of metal oxide nanoparticles on LIG and the synergistic interactions between the metal oxide nanoparticles and the graphene led to a much-enhanced ORR activity. The enhancement benefits from the high surface area of LIG and the facilitation of electron transfer from electrode to metal oxide nanoparticles. For example, the presence of Co₃O₄, MoO_2 and Fe_3O_4 improves the $E_{1/2}$ to 0.79, 0.77, and 0.74 V (Figure 10a) and the electrons of ORR process to 3.6, 3.9, and 3.9 e^- , respectively (Figure 10b-d). Although the metal loading is <1 atom %, these metal oxides containing LIG hybrid materials can catalyze the ORR at a performance comparable to that of scarce platinum.¹⁶

4.3. Overall Water Splitting

The ex situ electrodeposition method provides an effective and efficient way to expand the deposited materials on LIG beyond oxides.^{20,30} Here, cobalt phosphorus (Co-P) and nickel–iron hydroxides (NiFe) were electrodeposited onto the LIG surface to work as the hydrogen evolution reaction (HER) electrode and oxygen evolution reaction (OER) electrode, respec-



Figure 13. LIG film for microbial antifouling. (a) Biofilm growth on the PI, graphite, and LIG surfaces with *P. aeruginosa* showing biomass and average thickness. Representative IMARIS software images for (b) PI; (c) graphite; (d) LIG; (e) the interface between the LIG (left) and PI film (right). Green represents live bacteria, red represents dead bacteria, and blue represents EPS. Reproduced with permission from ref 38. Copyright 2017 American Chemical Society.



Figure 14. Human finger motion detection with stretchable carbon traces. (a, b) Photograph of five stretchable strain sensors attached to the finger joints on the glove. (c) Relative resistance change of the strain sensors at different bending stages over time; the corresponding finger configuration for each plot region (i)—(ix) is shown in the snapshots below the plot. Reproduced with permission from ref 39. Copyright 2015 American Chemical Society.

tively.^{20,30} Two designs have been reported, one is fabricated on the two sides of a PI sheet (Figure 11a,b), and the other is made on a wood surface (Figure 11c). In comparison with the materials electrodeposited on glassy carbon, the HER electrode made on the LIG surface have lower onset overpotentials and higher current densities at the same overpotentials due to the higher surface area and the metal-enhanced synergistic effect (Figure 11d).²⁰ The HER and OER electrodes are able to deliver high current densities at low overpotentials and the Tafel slopes reach 35 and 78 mV dec⁻¹, respectively (Figure 11d,e).²⁰ Durability test shows that the electrodes made on LIG surfaces are stable for catalyzing the overall water splitting (Figure 11f).²⁰

4.4. Water Treatment

LIG is employed as a membrane for separation by taking advantage of its superhydrophobicity property.^{18,37} A LIG filter is prepared by first generating ~100 μ m holes in the PI sheet at high laser power and then lasing the PI in an Ar atmosphere to afford a superhydrophobic surface (Figure 12a–c). Figure 12d–f demonstrates the experiment of water–oil separation.¹⁸ The superhydrophobic LIG membrane can also be used for desalination with an air gapped distillation process as demonstrated by Tittle et al.³⁷

Another use of LIG for water treatment is the prevention of microbial fouling and the exertion of antimicrobial action (Figure 13).³⁸ *Pseudomonas aeruginosa* was used as the species for biofilm study. Both living *P. aeruginosa* and extracellular polymeric substance (EPS) were rarely observed on the LIG surface (Figure 13a and d). However, both control samples, PI and graphite, are clearly covered by a biofilm (Figure 13a–c).³⁸ The antifouling property of LIG benefits from its zeta potential and the hydrophilic surface.³⁸ It also might arise from its superhydrophilic properties where water is not easily displaced from the surface.

4.5. Sensors from LIG

Rahimi et al. developed sensitive unidirectional strain sensors by embedding LIG into cured elastomers such as poly-(dimethylsiloxane).³⁹ These strain sensors could be placed on gloves that tracked the positions of the fingers of a wearer, as shown in Figure 14. The sensors did not degrade upon stretching multiple times. The conductivity of the sensor dropped as the sensor was twisted or stretched, providing a measurable response to movements of the glove fingers. Similar sensors were fabricated from LIG by Luo et al.⁴⁰

5. SUMMARY AND OUTLOOK

In this Account, a facile and cost-effective approach for the synthesis of 3D porous graphene has been demonstrated. This technique has been further developed to engineer its properties such as its morphology, composition, and surface area. Two strategies have been proposed for the scalable production of LIG: the roll-to-roll in-plane architecture and the macroscopic 3D printed structure. With worldwide research efforts, LIG has found broad applications in microfluidics, renewable energy devices, sensors, water purification, and many other fields.^{15,16,18,25,27,28} LIG has spawned wide academic interest, and it is being rapidly applied to industrial applications. Future development of the technique will include the design and optimization of LIG-based composites for other diverse applications. This includes sensing, catalysis, and energy storage devices. Additionally, there will be the development of LIG from natural products for fabrication of biodegradable devices to reduce electronic waste,⁴¹ and the synthesis of other carbon allotropes such as diamond, fullerenes, and carbon nanotubes.⁴² With these burgeoning advancements and the gaining worldwide research interest, the rapid transfer of LIG from laboratory to commercial products is foreseen.

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Notes

The authors declare the following competing financial interest(s): Some of the authors are co-inventors on Rice University owned intellectual property that is in the process of being licensed. Conflicts of interest are managed through regular disclosure to the Rice University Office of Sponsored Programs and Research Compliance.

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