Laser Direct-Writing

# Laser-Reduced Graphene: Synthesis, Properties, and Applications

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Laser reduction of graphene oxide has attracted significant interest in recent years, because it offers a highly flexible, rapid, and chemical-free graphene fabrication route that can directly write on almost any solid substrate with down to sub-micrometer feature size. Laser-reduced graphene (LRG) is explored for various important applications such as supercapacitors, sensors, field effect transistors, holograms, solar cells, flat lenses, bolometers, thermal sound sources, cancer treatment, water purification, lithium-ion batteries, and electrothermal heaters. This contribution reviews most recent research progress on the aspects of fabrication, properties, and applications of LRG. Particular attention is paid to the mechanism of LRG formation, which is still debatable. The three main theories, including the photochemical process, the photothermal process, and a combination of both processes, are discussed. Strategies for tuning the properties and performance of LRG, such as the laser parameters, chemical doping, structure modulation, and environment control, are highlighted. LRGs with better performance including smaller feature size, higher conductivity, and more flexible morphology design in both 2D and 3D formats will offer tremendous opportunities for advancement in electronics, photonic, and optoelectronic applications.

# 1. Introduction

Graphene is a flat monolayer of carbon atoms tightly packed into a 2D honeycomb lattice.<sup>[1]</sup> Graphene has attracted tremendous attention because of its unique properties including high electrical and thermal conductivities, optical transparency, and mechanical strength, which are highly desirable in a broad range of applications.<sup>[2–4]</sup> Therefore, it is of great importance to develop effective fabrication methods for high-quality graphene.<sup>[5]</sup> A variety of methods have been employed to directly

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produce graphene with relatively high crystalline quality, including mechanical exfoliation of graphite,<sup>[6,7]</sup> epitaxial growth,<sup>[8-10]</sup> and chemical vapor deposition (CVD).<sup>[11-14]</sup> Another class of methods adopts graphene oxide (GO) as the precursor for the synthesis of graphene with varied qualities. GO can be reduced to graphene by various reduction routes such as thermal,<sup>[15,16]</sup> chemical,<sup>[17–19]</sup> electrical,<sup>[20]</sup> microwave,<sup>[21]</sup> photo,<sup>[22,23]</sup> laser,<sup>[24]</sup> or a combination of these methods.<sup>[25]</sup> Table 1 summarizes several typical reduction methods for graphene oxide and the respective conductivity (or sheet resistance) of reduced graphene, which is related to the reduction quality and defect density.<sup>[26]</sup>

Among these techniques, laser reduction is considered very promising for graphene devices<sup>[27]</sup> including supercapacitors,<sup>[28–31]</sup> sensors,<sup>[32–35]</sup> field effect transistors (FETs),<sup>[36–38]</sup> thin film transistors,<sup>[39]</sup> holograms,<sup>[40]</sup> solar cells,<sup>[41–46]</sup> and flat lenses.<sup>[47]</sup> During laser reduction, the precursors, typically a GO film, are irradiated with the laser

and converted in situ into reduced graphene oxide (rGO). Besides the reduction of pure GO, doped GO can also be produced with laser irradiation. This method eliminates the use of highly corrosive and toxic chemicals, and avoids the requirement for high temperatures.<sup>[48]</sup> This process is also compatible with substrates that cannot tolerate high temperatures including polymers. Moreover, the laser writing process can achieve localized reduction of GO and is highly flexible in micropattern creation, which makes laser reduction very suitable for microdevice fabrication. The record feature size of laser direct-writing technology to date is down to

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 $0.55~\mu m.^{[40]}$  The whole process of laser reduction can be completed in several minutes,^{[49]} which greatly improves the efficiency of production.

Recently, there have been many new developments on the subject of laser reduction for synthesis of graphene. This report aims to summarize the recent developments in this active field. Particular attention is paid to the precursor material for laser reduction, the mechanisms of laser reduction, and the diverse range of applications of this technology.

In the published literature, different precursors, mainly GO and polymers, were used for laser reduction. After laser irradiation, the resulting graphene materials are referred variously in different papers as laser-induced graphene,<sup>[29]</sup> laser-scribed graphene,<sup>[49]</sup> or simply reduced graphene oxide.<sup>[28]</sup> The term laser-reduced graphene (LRG) is adopted throughout this paper.

# 2. Laser Reduction with Various Precursors

# 2.1. Graphene Oxide

As a typical precursor of LRG, GO contains only one or a few layers of carbon atoms with a similar structure to graphene, but the plane of carbon atoms in GO is decorated with oxygen-containing groups.<sup>[50]</sup> Due to its oxygen-containing groups, it is highly hydrophilic and can form stable aqueous colloids,<sup>[51,52]</sup> which enables convenient, solution-based processes for industrial production. On the other hand, the presence of oxygenated groups on the basal plane also disrupts the  $\pi$ - $\pi$  conjugation, making GO an electrical insulator.<sup>[53]</sup>

GO can be produced from graphite on a large scale with costeffective chemical methods.<sup>[54]</sup> Several different methods are employed for GO synthesis, including the Brodie method,<sup>[55]</sup> the Staudenmaier method,<sup>[56]</sup> and the Hummers method,<sup>[57]</sup> or their modifications. Among these methods, the modified Hummers method (MHM) is the most commonly used approach for GO fabrication.<sup>[50]</sup> The raw material for MHM synthesis is graphite,

 Table 1. Typical techniques for reduced graphene and their properties.





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which consists of closely stacked individual graphene layers. After the graphite is mixed with concentrated sulfuric acid  $(H_2SO_4)$ , sodium nitrate (NaNO<sub>3</sub>), and potassium permanganate

Technique	Key procedure	Conductivity/Resistivity	Ref.
Thermal reduction	GO annealing at 1100 °C	$5.5  imes 10^4 \text{ S m}^{-1}$	[122]
	GO annealing at various temperatures	$1.78  imes 10^3$ S m <sup>-1</sup>	[131]
Chemical Reaction	Hydrazine reduction of GO	$2 \times 10^2 \text{ S m}^{-1}$	[17,132]
	Hydroiodic acid reduction of GO	$2.98\times10^4~S~m^{-1}$	[133]
Electrical reduction	ctrical reduction Reducing GO using electrical stimulus		[20]
Microwave reduction	GO annealing at 300 °C for 1 h under argon, then microwaved for 1–2 s under argon	-	[21]
Electron beam lithography	Reducing GO with focused electron beam	-	[134]
Photoreduction	UV irradiation on the ${\rm TiO}_2$ and GO mixture	$4.6\times 10^6~\Omega~\text{sq}^{-1~\text{a})}$	[135]
	Camera flash on GO and polymer mixture	-	[23]
Combined method	Hydrazine reduction and thermal annealing at 1100 $^\circ C$	$5.5  imes 10^4 \ \mathrm{S} \ \mathrm{m}^{-1}$	[136]
	Hydrazine reduction and thermal annealing at 1100 $^{\circ}\mathrm{C}$	10 <sup>4</sup> S m <sup>-1</sup>	[25]
Laser reduction	Laser direct irradiation on GO	$2.56\times10^4~S~m^{-1}$	[24]

<sup>a)</sup>Film thickness data unavailable for unit conversion.



(KMnO<sub>4</sub>), its graphene layers are mainly oxidized by the active oxidizing agent, typically dimanganese heptoxide (Mn<sub>2</sub>O<sub>7</sub>), which results from the reaction of KMnO<sub>4</sub> with H<sub>2</sub>SO<sub>4</sub>.<sup>[58,59]</sup> The addition of NaNO<sub>3</sub> further increases the interlayer distance between graphene sheets and enhances the oxidation.<sup>[60]</sup>

Dimiev and Tour carried out a comprehensive study on the formation mechanism of GO from graphite.<sup>[52]</sup> **Figure 1**a illustrates that the process of GO synthesis consists of three main steps: the penetration of  $H_2SO_4$ , the oxidization of the graphite, and exfoliation in sonication water. The structure of GO is portrayed as a graphene sheet bonded to oxygen functional groups, including carboxyl, hydroxyl, and epoxy groups, as illustrated in Figure 1b.<sup>[61]</sup>

#### 2.2. Laser Reduction of GO Film

#### 2.2.1. Pure GO Film

GO film can be conveniently produced from GO colloid with several different techniques, such as spraying, drop-casting,

and spin-coating. With laser irradiation, the GO film can be reduced in air at room temperature.<sup>[62]</sup> Furthermore, the LRG microcircuits can also be fabricated via direct laser patterning on GO films, shown in Figure 2a-c.<sup>[24]</sup> Figure 2d illustrates the atomic force microscopy (AFM) characterization of laserreduced GO film and the sunken surface resulted from laser treatment. The percentage of decreased thickness varies from 33.3% to 83.3% in different publications as shown in Table 2. Zhang et al. demonstrated that the sink of the laser-scribed area resulted from the mass loss of the GO films and rearrangement of the carbon atom.<sup>[24]</sup> Another explanation for the sunken surface is the ablation induced by the laser,<sup>[62]</sup> which can heat the top layers of GO to a temperature above 500 °C and burn them off.<sup>[63]</sup> Figure 2e-g shows the Raman spectra of various layers of graphene on quartz, highly oriented pyrolytic graphite (HOPG), GO, and GO reduced with different lasers at various atmospheres, respectively. The D-band and G-band on a Raman spectrum result from vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite and  $E_{2\sigma}$ phonon scattering of graphitic structure, respectively.<sup>[64]</sup> Raman



**Figure 1.** a) Schematic illustration of bulk graphite conversion into GO. Reproduced with permission.<sup>[52]</sup> Copyright 2014, American Chemical Society. b) Schematic illustration of a typical GO chemical structure. Reproduced with permission.<sup>[61]</sup> Copyright 2009, Nature Publishing Group.



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**Figure 2.** a) Illustration of laser-reduced GO microcircuit fabrication. b,c) Optical microscopy images of microcircuit; scale bars, 10  $\mu$ m. d) AFM of laser-reduced GO films and height profile along the white line (L1). a–d): Reproduced with permission.<sup>[24]</sup> Copyright 2010, Elsevier. e) The Raman spectra of monolayer, bilayer, three layer, and four layer graphene on quartz. Reproduced with permission.<sup>[65]</sup> Copyright 2008, American Chemical Society. f)The Raman spectra of HOPG and GO flake. g) The Raman spectra of GO treated with different lasers at various atmospheres: CW (20 mW at 532 nm) in air and N<sub>2</sub>, and pulsed (5 mJ per pulse, 9 ns, 20 Hz) 532 and 355 nm laser in N<sub>2</sub>. f,g) Reproduced with permission.<sup>[66]</sup> Copyright 2010, American Chemical Society. h) Schematic setup of the laser reduction of GO in an oxygen-free sealed chamber. Reproduced under the terms of the Creative Commons Attribution 4.0 International license.<sup>[71]</sup> Copyright 2016, the authors, published by Nature Publishing Group.

spectroscopy of graphene materials provides useful information on the defects (D-band), in-plane vibration of  $sp^2$  carbon atoms (G-band), as well as the stacking orders (2D-band).<sup>[65]</sup> The symmetry and sharpness of 2D-band have been used for determining graphene thickness. Compared to graphene and graphite, GO demonstrates a broad and strong D-band www.advancedsciencenews.com

 Table 2. The decrease of film thickness by laser treatment.

Film thickness before laser treatment [nm]	Film thickness after laser treatment [nm]	Percentage of thickness decrease [%]	Ref.
15	10	33.3	[121]
32	16	50.0	[63]
55	25	54.5	[24]
60	10	83.3	[62]

at 1345 cm<sup>-1</sup> and its 2D-band is nearly absent.<sup>[66]</sup> Depending on the laser and environment, varied degree of change can be noticed after laser treatment: the reduction of D-band, the sharpening of G-band, and the appearance of 2D-band, which shows the reduction of GO with the ratio of  $I_D/I_G$  providing a quantitative measure on degree of reduction. After laser reduction, the conductivity of LRG can be improved to 2.56 × 10<sup>4</sup> S m<sup>-1</sup>,<sup>[24]</sup> while the conductivity of GO typically ranges from 5 × 10<sup>-4</sup> to 4 × 10<sup>-1</sup> S m<sup>-1</sup>,<sup>[18,67]</sup> However, this conductivity of LRG is still much lower than that of graphene (10<sup>8</sup> S m<sup>-1</sup>) fabricated with mechanical exfoliation.<sup>[68]</sup> or CVD.<sup>[69]</sup> This relatively low conductivity results from defects of LRG and resistance between stacked LRG layers.<sup>[70]</sup>

Instead of exposing the whole process to ambient conditions, to achieve high-quality LRG, Sokolov et al. conducted laser reduction of GO film in an oxygen-free environment (vacuum or N<sub>2</sub> atmosphere).<sup>[26]</sup> After laser reduction, the C/O ratio increased from 2.43 (GO) to 40 (LRG), which indicates tremendous oxygen removal and a high degree of reduction. Similarly, Guan et al. conducted laser reduction of GO film in a liquid N<sub>2</sub> environment (schematic setup illustrated in Figure 2h).<sup>[71]</sup> Due to the suppression of heating expansion and frozen effect, the LRG prepared in liquid N<sub>2</sub> atmosphere demonstrates more orderly states, fewer defects, and high conductivity ( $\approx 7.27 \times 10^2$  S m<sup>-1</sup>, two orders of magnitude higher than that of LRG in N<sub>2</sub> atmosphere).

In addition to the environment, the reduction is also dependent on laser parameters. Petridis et al. reported that the laser fluence should be greater than the minimum fluence (10–15 mJ cm<sup>-2</sup> for 248 nm pulse laser) that can initiate the reduction of GO, while remaining lower than the critical fluence level (80 mJ cm<sup>-2</sup> for 248 nm pulse laser), which can cause damage to the GO sheets.<sup>[48]</sup> Using the heat conduction equation, it is concluded that the pulse frequencies, pulse temporal widths, and laser energy distributions all affect the photothermal effect of lasers,<sup>[72]</sup> which plays an important role in laser reduction.<sup>[37]</sup> We will further expand the discussion on influence of laser parameters in Section 3.

Using a two-beam interference laser, Wang et al. fabricated periodic grating structures and simultaneously removed the oxygen groups on the GO film.<sup>[73]</sup> The water contact angle of the GO film treated by laser can be changed by modulation of laser power (from 68.7° to 156.7°) due to the surface topography and the chemical components. With a large contact angle, water droplets were still attracted to the surface while the surface was inverted. This LRG with high adhesion has great potential for novel microfluidic devices.

Laser reduction is a very localized process which does not affect the flexibility of the underlying substrates.<sup>[74]</sup> This

reduction process is compatible with inexpensive, recyclable, temperature-sensitive substrates including plastics.<sup>[48]</sup> Deng et al. reported synthesis and patterning of LRG from GO films on diverse substrates, including leaves, lenses, and fabrics.<sup>[75]</sup>

## 2.2.2. GO-Based Composites Films

In order to achieve higher electrical conductivity, Kumar et al. mixed GO with gold and platinum salts (HAuCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub>) individually and reduced the films by laser.<sup>[76]</sup> With laser irradiation, platinum or gold salts were simultaneously reduced to metal due to photolysis. The reduced metal aggregated to form metal nanoparticles, which deposited onto the surface of the LRG, and the conductivity of the metal-decorated LRG is about four times higher than the undecorated LRG. With a similar method, Li et al. reported that the conductivity of LRG decorated with Au nanoparticles has been increased to  $1.1 \times 10^6$  S m<sup>-1</sup>, two orders of magnitude larger than that of LRG.<sup>[77]</sup> The improved conductivity is due to the highly conductive Au nanoparticles bridging the gaps between the LRG sheets. Figure 3a,b illustrates the laser writing of GO/HAuCl<sub>4</sub> on a paper substrate and LRG with Au nanoparticles after laser treatment. Furthermore, Ryu et al. reported that the LRG doped with nitrogen was made from GO coated on GaN by laser irradiation.<sup>[78]</sup> It was revealed that the nitrogen dopant originated from the GaN substrate, which decomposed during the laser treatment. The N-doped LRG achieved a very low sheet resistance of 120  $\Omega$  sg<sup>-1</sup> in comparison to  $1.1 \times 10^8 \Omega$  sg<sup>-1</sup> for the undoped LRG.

#### 2.3. Laser Reduction of GO Suspension

#### 2.3.1. Pure GO in Solution

Parallel to solid state GO, GO suspended in solution can also be reduced by laser irradiation.<sup>[79-81]</sup> Abdelsayed et al. reported the synthesis of LRG from GO in water with lasers under ambient



**Figure 3.** a) Schematic illustration of laser writing of GO/HAuCl<sub>4</sub> on a paper substrate. b) The illustration of LRG with Au and its scanning electron microscopy (SEM) image. a,b) Reproduced with permission.<sup>[77]</sup> Copyright 2016, Royal Society of Chemistry.

conditions.<sup>[82]</sup> In the experiment, both 532 nm (7 W) and 355 nm (5 W) lasers efficiently converted GO in solution to rGO. However, for a 1064 nm laser with similar power (5–7 W), no reduction of GO could be observed due to the reduced IR absorption of the GO. Huang et al. reported the reduced IR absorption of solution by irradiation of a 248 nm KrF excimer laser, as shown in **Figure 4a**.<sup>[5]</sup> Upon irradiation, the yellow–brown GO solution turned black in several minutes, which indicates GO reduction. It was also revealed that, after the removal of most oxygen-containing groups with laser reduction, the thickness of LRG sheets is almost the same as that of GO sheets (1.1 nm) by AFM characterization, as shown in Figure 4b,c.

In addition, Ibrahim et al. introduced the production of LRG gels by focusing a femtosecond (fs) laser at the interface of an air/GO solution.<sup>[83]</sup> The surface roughness of the film produced from LRG gels can be less than 6 nm, while that from LRG in solution is 25.3 nm. Figure 4d,e shows the schematic diagram of laser focusing within the GO solution and at the air/liquid interface, respectively. Figure 4f illus-trates GO sheets in solution with oxygen functional groups, which break into smaller fragments accompanied with the removal of the oxygen functional groups upon laser irradiation as shown in Figure 4g. Figure 4h shows the aggregation of the reduced GO sheet fragments, which result in the formation of a gel.

## 2.3.2. GO-Based Composites in Solution

Apart from pure GO solution, nanometals were mixed into GO solution for reduction.<sup>[84,85]</sup> Zedan et al. reported that gold nanoparticles were anchored to the surface of LRG for potential application as a photothermal energy convertor by laser irradiation on a mixture suspension of Au nanoparticles and GO.<sup>[86]</sup> After the laser treatment, the gold nanoparticles were found to adhere at the defects and vacancies on the large surface of LRG. The coupling of surface plasmon resonance of the gold nanoparticles with LRG enhances the efficiency of photothermal energy conversion, which may be used for enhancing the efficiency of heating or evaporating liquid with solar energy. Tan et al. reported synthesis for N-doped graphene quantum dots (NGQDs) by laser irradiating GO in an aqueous ammonia solution.<sup>[87]</sup> Under irradiation, the graphene nanosheet can be cut into small pieces likely due to laser-induced radicals with simultaneous nitrogen doping. The NGQDs exhibit strong and tunable fluorescence, demonstrating potential application in microoptoelectronic devices.

# 2.3.3. Comparison of GO Film and GO Solution

Compared with laser reduction of GO thin film, which is suitable for microdevice applications, laser reduction of a GO solution appears to be more ready for upscaling. Moreover, producing graphene composites by premixing GO with other additions by laser treatment has its particular appeal as a rapid and neat modification process.<sup>[5]</sup>

# 2.4. Laser Reduction of Polymers and Biomass

As early as in the 1990s, pulsed ultraviolet lasers were used to irradiate polyimide (PI) film, producing porous carbon material with high conductivity (10<sup>3</sup> S m<sup>-1</sup>).<sup>[88–90]</sup> Ingram et al. attempted this laser carbonized polyimide for humidity sensors.<sup>[91]</sup> However, it was not presented as a significant method for graphene fabrication. In 2014, Tour and co-workers reported porous graphene films' fabrication from commercial polymer films using a CO<sub>2</sub> laser.<sup>[29]</sup> In their research, 15 kinds of polymers were treated with the laser, but only Kapton polyimide and Ulse polyetherimide, which contain aromatic and imide repeat units, could be reduced to graphene. Figure 5a-d shows the patterning on PI by laser and its SEM images. The LRG fabricated from PI exhibits high electrical conductivity  $(2.5 \times 10^3 \text{ S m}^{-1})$ , and can function as interdigitated electrodes of in-plane supercapacitors with a flexible laser patterning system. By irradiating both sides of PI sheets with a laser and stacking these sheets, the same group reported the fabrication of vertically stacked supercapacitors, which shows high-density energy storage while maintaining flexibility.<sup>[92]</sup> To further improve the performance of supercapacitors, Tour and co-workers deposited pseudocapacitive materials, which provide pseudocapacitance from surface redox reactions on electrodes.<sup>[93]</sup> The PI was converted to interdigitated porous LRG as electrodes of the capacitor by a CO<sub>2</sub> laser. Furthermore, a pseudocapacitive material, including manganese dioxide (MnO<sub>2</sub>), ferric oxyhydroxide (FeOOH), or polyaniline (PANI), was electrodeposited on the LRG, forming LRG-MnO<sub>2</sub>, LRG-FeOOH, or LRG-PANI composites. In this manner, the areal and volumetric specific capacitances of LRG-MnO<sub>2</sub> capacitors can be improved to 934 mF cm<sup>-2</sup> and 93.4 F cm<sup>-3</sup>, respectively, in comparison to those of LRG capacitors, namely 0.8 mF cm<sup>-2</sup> and 0.2 F cm<sup>-3</sup>, respectively. After 6000 cycles, the LIG-MnO<sub>2</sub> and LIG-PANI capacitors have high capacitance retention of 82% and 97%, showing good cycling stabilities.

Tour and co-workers also reported boron-doped LRG from PI mixed with H<sub>3</sub>BO<sub>3</sub> by a CO<sub>2</sub> laser shown in Figure 5e.<sup>[94]</sup> Within the boron-doped graphene structure, the Fermi level was shifted toward the valence band, enhancing charge storage and transfer. The capacitors with boron-doped LRG electrodes showed three times larger area capacitance and five to ten times larger volumetric energy densities than those of nondoped LRG electrodes. With a similar method, they published the preparation of nanocrystals embedded in LRG.<sup>[95]</sup> A precursor of  $Co_3O_4$ , MoO<sub>2</sub>, or Fe<sub>3</sub>O<sub>4</sub> was individually mixed into poly(pyromellitic dianhydrideco-4,4 -oxidianiline amic acid) solution for PI synthesis. After laser irradiation of these mixtures, the metal nanocrystals were embedded in the porous graphene structure. With a metal content of less than 1%, these materials exhibit excellent oxygen reduction catalytic activity. By varying the metal element, the performance of metal embedded LRG is tunable, which is useful for various applications, including the hydrogen evolution reaction and oxygen evolution reaction. This group also modulated the wetting properties of LRG derived from PI by controlling the laser reduction atmosphere.<sup>[96]</sup> The water contact angle on the LRG fabricated under different atmospheres can be tuned from  $0^{\circ}$  (in O<sub>2</sub> or air) to >150° (in Ar or H<sub>2</sub>) (the contact angle of the lotus leaf is about 161°[97]) due to surface morphology and the chemical composition of LRG.







**Figure 4.** a) Illustration of laser-reduced GO in solution, before (on the left) and after (on the right) laser irradiation. b,c) AFM images of b) GO and c) pulsed laser irradiated GO dispersion in water ( $0.05 \text{ mg mL}^{-1}$ ) after their deposition on a freshly cleaved mica surface through dropcasting method. a–c) Reproduced with permission.<sup>[5]</sup> Copyright 2011, Elsevier. d,e) Schematic diagram of d) laser focus within the GO solution and e) laser focusing at air/liquid interface. f–h) Schematic diagram of the femtogel formation: f) GO sheets in solution; g) the laser beam strikes the GO sheets producing smaller fragments with pristine edges free from carboxyl and hydroxyl groups; h) aggregation of the reduced GO sheet fragments after removing functional groups, resulting in femtogel formation. d–h) Reproduced with permission.<sup>[83]</sup> Copyright 2016, John Wiley and Sons.

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**Figure 5.** a) Schematic illustrate of laser patterning on PI. b) SEM image of the pattern. c) SEM image of LRG on the PI substrate; scale bar, 10 µm. Inset is the corresponding higher magnification SEM image; scale bar, 1 µm. d) Cross-sectional SEM image of the LRG on the PI; scale bar, 20 µm. Inset is the SEM image; scale bar, 1 µm. a–d) Reproduced with permission.<sup>[29]</sup> Copyright 2014, Nature Publishing Group. e) Synthetic scheme for the preparation of borondoped LRG. Reproduced with permission.<sup>[94]</sup> Copyright 2015, American Chemical Society. f–i) SEM images of cross-sectional morphologies of the line the laser fabricated at varied powers: f) P = 2.5 W, g) P = 3.5 W, h) P = 5.5 W, and i) P = 7.5 W. The laser scanning speed is 63.5 mm s<sup>-1</sup>. The beam size of the laser is ≈100 µm; scale bar, 100 µm. f-i) Reproduced with permission.<sup>[32]</sup>

Based on the same PI and similar process, Luo et al. studied the effect of laser power and scanning speed on the piezoresistive sensitivity of the LRG sensors.<sup>[32]</sup> Figure 5f–i presents ADVANCED MATERIALS TECHNOLOGIES www.advmattechnol.de

the SEM images of the cross section of laserscribed lines with different laser power. It can be observed that the LRG is only on the top surface of the PI film and the laser-irradiated region protrudes from the PI. The thickness of the protruded structure increases with enhanced laser power.

Laser reduction of PI to graphene is already commercialized and ready for roll-toroll production.<sup>[29]</sup> This simple and flexible fabrication process is very suitable for largescale fabrication of flexible electronics at low cost. However, a few groups are studying and reporting LRGs from polymer, and its application research mainly focuses on capacitors and strain sensors. LRG from PI demonstrates many unique properties and has great potential for many other applications.

In addition, Tour and co-workers also demonstrated that natural wood can be transformed into graphene directly by irradiation with laser in an inert atmosphere.<sup>[98]</sup> Different types of wood including pine, birch, and oak were studied, and it was discovered that both the aromatic lignin content and the inherent composite structure of the wood influence the formation of LRG. Several applications including supercapacitors and water splitting were demonstrated with the LRG fabricated from wood.

# 3. The Mechanism of Laser Reduction

The mechanism of laser reduction has been widely discussed in the literature.<sup>[5,29,37,40,99–102]</sup> Three main mechanisms have been proposed including the photothermal effect,<sup>[29]</sup> photochemical effect,<sup>[40]</sup> or a combination of the two.<sup>[37,99]</sup> Smirnov et al. claimed the threshold of GO photoreduction was 3.2 eV (about 390 nm).<sup>[100]</sup> This means that it is only possible to reduce GO through the photochemical process for a laser with a wavelength shorter than 390 nm; and for a laser with a wavelength longer than 390 nm, the reduction of GO is caused by the photothermal effects of the laser irradiation. Meanwhile, it was found that exothermic reduction of GO occurs at a temperature between 200 and 230 °C.<sup>[103,104]</sup> Lin et al. further explored this mechanism and proposed that photochemical processes tend to occur in lasers with short wavelengths and ultrashort pulse widths.<sup>[29]</sup> For a laser with long wave-

length (10.6  $\mu$ m) and long pulse width (14  $\mu$ s), the energy from laser irradiation results in extremely high localized temperatures (>2500 °C), which could easily break the bonds including

C-O, C=O, and C-N bonds. However, other studies indicate that the photochemical process is mostly accompanied by heating, which results in the thermal reduction of GO, regardless of the differences in wavelength. Guo et al. attributed GO reduction to both photochemical and photothermal effects induced by a laser.<sup>[37]</sup> In their view, for a femtosecond laser, the laser irradiation would result in electronic excitation during the first several picoseconds, then C-O bonding weakening and eventually the oxygen removal, which is considered as a photochemical process. Due to the recombination of electrons and holes (\$100 ps), intensive heat would be subsequently generated and finally induce thermal reduction. This explanation agrees with Arul et al.'s work. Arul et al. employed three different lasers (800 nm, fs pulses; 248 nm, nanosecond (ns) pulses; and 788 nm, continuous wave) to reduce the same GO film under the same conditions.<sup>[99]</sup> By comparing the results of GO reduction with different lasers, a two-step reduction process was proposed. First, the photochemical removal of oxygen was realized on the surface. Second, the reduced carbon was restored to graphene structure thermally.

To identify whether a thermal process was introduced during laser irradiation, Li et al. utilized a temperature measurement method by monitoring the spectral shift of CdSe nanoparticles, which were mixed into the GO film.<sup>[40]</sup> The measurement pointed to that an athermal process was responsible for the single femtosecond pulse laser reduction (wavelength, 800 nm; pulse width, 100 fs), because no notable spectral shift of CdSe nanoparticles could be observed during the laser irradiation. The photochemical reduction of laser wavelength (800 nm) at first appears to contradict the wavelength threshold theory of photochemical reduction (less than 390 nm). However, considering the likelihood of multiphoton absorption, the wavelength threshold of the laser may be relaxed. This result is consistent with the findings of Zhang and Miyamoto through first-principles simulations, which show that for the femtosecond laser, no significant heating was generated, and the oxygen groups on graphene sheets could be completely removed upon laser irradiation.[101]

From the above discussion, it can be concluded that the mechanism of laser reduction varies with different wavelengths of lasers. For lasers with a long wavelength ( $\gg$ 390 nm), the reduction process mainly relies on the photothermal process. For those with a short wavelength (<390 nm), the photochemical process is always accompanied with thermal generation. Furthermore, the threshold of photochemical reduction needs to be redefined, considering multiphoton processes.

Specifically for GO in solution with laser irradiation (248 nm), the temperature of GO solution can only rise to 50–60 °C, which is not sufficient for thermal reduction. Therefore, there is speculation that reduction of GO in solution is mainly a photochemical process.<sup>[105]</sup> However, with a 248 nm laser, Huang et al. suggested that, although the temperature of the solvent only reaches about 40 °C during laser irradiation due to the existence of solvent, the temperature of the GO flake can still be raised above 200 °C, which results in thermal deoxygenation reaction.<sup>[5]</sup> Additionally, Muttaqin el al. also proposed that the GO in solution may also be reduced by solvated electrons from water molecules excited by intense laser pulses (80 mJ cm<sup>-2</sup>).<sup>[102]</sup>

Table 3 summarizes the key parameters for used lasers and resultant LRG qualities as reported by various studies. For the reduction of GO film, both continuous wave lasers and pulse lasers have been employed. Lasers with different wavelengths. powers, temporal pulse widths, and repetitions can all achieve reduction of GO film. It should be noted in most of the reports the spot size of the laser was not reported; therefore, we are unable to unify these parameters with laser fluence. It can be noticed that the conductivity of GO, the precursor material, varies substantially among different groups ranging from 10<sup>1</sup> to 10<sup>4</sup> S m<sup>-1.[106,107]</sup> Since conductivity measurement is subject to the specific setup, quality of contacts, sample preparation etc., it would be somewhat unfair to compare the conductivities between different studies. Rather, it is the conductivity difference between pre- and post-treatment materials that matters. Strong et al. reported that the conductivity of GO was improved by as much as six orders of magnitude after laser reduction.<sup>[33]</sup> After the reduction of GO film, the ratio of D-band to G-band  $(I_{\rm D}/I_{\rm G})$  can be decreased from 0.82 to 0.27,<sup>[71]</sup> and the C/O ratio can be improved from 2.4 to 40.<sup>[26]</sup> For the reduction of GO solution, several pulse lasers with different wavelengths ranging from 248 to 800 nm were used. Compared to the reduction of GO film, the reduction degree of GO suspension is relatively low (C/O ratio = 7.4).<sup>[102]</sup> This relatively low reduction efficiency could be related to the energy absorption of water. Moreover, the GO in solution is surrounded with dissolved oxygen in water, which may also affect the degree of reduction. It is also worth noting that CO<sub>2</sub> laser was mainly employed for polymer reduction. After laser reduction of PI, the carbon ratio can be improved from 71% to 97%.

# 4. Applications

# 4.1. LRG-Based Supercapacitor

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have received considerable attention worldwide because of their high power density (ten times more than batteries), fast charging (with seconds), long cycle life, which make them a promising candidate as the next-generation power devices.<sup>[108,109]</sup> Graphene is an attractive electrode material for supercapacitors due to its large theoretical surface area, high electrical conductivity, good mechanical properties, and chemical stability.<sup>[110]</sup> El-Kady et al. fabricated supercapacitors with LRG as electrodes on flexible polyethylene terephthalate (PET) substrates.<sup>[111]</sup> The LRG shows high electrical conductivity (1738 S m<sup>-1</sup>) and specific surface area (1520 m<sup>2</sup> g<sup>-1</sup>). The supercapacitors with LRG electrodes exhibit high power density (20 W cm<sup>-3</sup>) and excellent cycle stability retaining 96.5% of its initial capacitance after 10 000 cycles. With a similar approach, El-Kady and Kaner demonstrated a scalable fabrication of supercapacitors by laser direct writing on GO films using a standard LightScribe DVD burner.<sup>[49]</sup> More than 100 micro-supercapacitors were produced in 30 min or less. Gao et al. also demonstrated scalable supercapacitor fabrication by the laser reduction and patterning of GO free-standing films.<sup>[28]</sup> As shown in Figure 6a-e, the LRG functions as electrodes of inplane or conventional sandwich supercapacitor. The GO serves

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# Table 3. Laser parameters and reduction degree of LRGs.

Material	Laser	CW/pulse	Laser parameters	Reduction degree	Conductivity/Resistance	Ref.
GO film	Diode laser 532 nm	CW <sup>a)</sup>	P <sup>b)</sup> :12 mW	C—C: 55.3%, <i>I<sub>D</sub>/I<sub>G</sub></i> :0.97 (GO) C—C: 69.2%, <i>I<sub>D</sub>/I<sub>G</sub></i> :0.96 (LRG)	$\approx$ 7.4 S m <sup>-1</sup> (GO) ≈3.6 × 10 <sup>3</sup> S m <sup>-1</sup> (LRG)	[63]
GO film	Fiber laser 1064 nm	ns	W <sup>c)</sup> :20 ns F <sup>d)</sup> : 10 kHz D <sup>e)</sup> : 4–28 J cm <sup>-2</sup>	C—C: 54.1%, <i>I<sub>D</sub>/I<sub>G</sub></i> :0.97 (GO) C—C: 78.6%, <i>I<sub>D</sub>/I<sub>G</sub></i> :0.82 (LRG)	-	[121]
GO film	KrF excimer laser 248 nm	ns	W: 25 ns F: 1 Hz D: 0.06–0.4 J cm <sup>-2</sup>	C/O: 2.41, I <sub>D</sub> /I <sub>G</sub> :0.51 (GO) C/O: 40, I <sub>D</sub> /I <sub>G</sub> :0.29 (LRG vacuum)	10 <sup>10</sup> Ω sq <sup>-1</sup> (GO) ≈100–500 Ω sq <sup>-1</sup> (LRG vacuum)	[26]
GO film	KrF excimer laser 248 nm	ns	W: 20 ns <i>F</i> : 1 Hz D: 0.08 J cm <sup>-2</sup>	C—C: 39%, I <sub>D</sub> /I <sub>G</sub> :0.79 (GO) C—C: 84%, I <sub>D</sub> /I <sub>G</sub> :1.0 (LRG)	-	[48]
GO film	Picosecond pulsed laser 1064 nm	ps	W: 10 ps F: 100 kHz D: 0.1 to 0.4 J cm <sup>-2</sup>	C/O: 2.4, I <sub>D</sub> /I <sub>G</sub> :0.82 (GO) C/O: 9.1, I <sub>D</sub> /I <sub>G</sub> :0.42 (LRG N <sub>2</sub> ) C/O: 10.3, I <sub>D</sub> /I <sub>G</sub> :0.27 (LRG liquid N <sub>2</sub> )	≈2 × 10 <sup>-3</sup> S m <sup>-1</sup> (GO) ≈4 S m <sup>-1</sup> (LRG N <sub>2</sub> ) ≈7.27 × 10 <sup>2</sup> S m <sup>-1</sup> (LRG liquid N <sub>2</sub> )	[71]
GO film	Femtosecond laser 800 nm	fs	W: 100 fs <i>F</i> : 1 KHz D: 1.2–4.8 nJ cm <sup>-2</sup>	C—C: 28% (GO) C—C: 54% (LRG)	-	[40]
GO film	Femtosecond laser 790 nm	fs	W: 120 fs F: 80 MHZ P: 0.5–3.5 mW	C—C: 44%, I <sub>D</sub> /I <sub>G</sub> :0.83 (GO) C—C: 61%, I <sub>D</sub> /I <sub>G</sub> :0.89 (LRG)	$2.56 \times 10^4$ S m <sup>-1</sup> (LRG)	[24]
GO film	Femtosecond laser 800 nm	fs	<i>W</i> : 120 fs <i>F</i> : 80 MHz	C−C: ≈45% (GO) C−C: ≈72%,, I <sub>D</sub> /I <sub>G</sub> :0.89 (LRG)	-	[62]
GO film	Femtosecond laser 515 nm	fs	<i>W</i> : 280 fs <i>F</i> : 500 kHz PE <sup>f)</sup> : 35–45 nJ	C/O: 1.26 (GO) C/O: 1.36 (LRG)	$\approx 10^4 \text{ S m}^{-1} \text{ (LRG)}$	[106]
GO film	Infrared laser 788 nm	-	<i>P</i> : 5 mW	C/O: 2.6 (GO) C/O: 27.8 (LRG)	≈ $6.6 \times 10^{-3} \text{ S m}^{-1} \text{ (GO)}$ ≈ $1.65 \times 10^3 \text{ S m}^{-1} \text{ (LRG)}$	[33]
GO film	CO <sub>2</sub> laser 10.6 μm	-	<i>P</i> : 1.9 W	I <sub>D</sub> /I <sub>G</sub> : 0.37 (LRG)	-	[112]
GO film	CO <sub>2</sub> laser 9300 nm	-	P: 4.8 W	C/O: 2 (GO) C/O: 10.1 (LRG)	$7.8 \times 10^1 \text{ S} \text{ m}^{-1}$ (LRG)	[107]
GO film	CO <sub>2</sub> laser	-	<i>P</i> : 2.4 W	C/O ≈ 2.3 (GO) C/O ≈ 9 (LRG)	$4.55\times10^2~S~m^{-1}$ (LRG)	[28]
GO solution	KrF excimer laser 248 nm	ns	W: 20 ns <i>F</i> : 50 Hz PE: 700 mJ	I <sub>D</sub> /I <sub>G</sub> : 1.03 (GO) I <sub>D</sub> /I <sub>G</sub> : 1.08(LRG)	$1.8 \times 10^4 \text{ S} \text{ m}^{-1}$ (LRG)	[5]
GO solution	Nd:YAG <sup>g)</sup> pulsed laser 532 nm	ns	<i>W</i> : 5 ns <i>F</i> : 10 Hz <i>P</i> : 0.3 W	C/O: 2, <i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub> : 1.5 (GO) C/O: 5, <i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub> : 1.3 (LRG)	$1.5 \times 10^{-4} \text{ S m}^{-1}$ (GO) $7 \times 10^2 \text{ S m}^{-1}$ (LRG)	[80]
GO solution	Femtosecond laser 800 nm	fs	<i>W</i> : 100 fs <i>F</i> : 300 Hz <i>D</i> : 10–140 mJ cm <sup>-2</sup>	C/O: 1.1, <i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub> : 0.97 (GO) C/O: 7.4, <i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub> : 0.83 (LRG)	33 S m <sup>-1</sup> (LRG)	[102]
GO solution	KrF excimer laser 248 nm	-	E <sup>h)</sup> : 300–530 mJ <i>F</i> : 10 Hz	C—C: 41.9% (GO) C—C: 76.2% (LRG)	-	[105]
Kapton PI	CO <sub>2</sub> laser 10.6 μm	ms	W: 14 ms P: 2.4–5.4 W	C: 71% (PI) C: 97% (LRG)	-	[29]
Kapton PI	CO <sub>2</sub> laser 10.6 μm	-	<i>P</i> : 1.5–7.5 W	C: 92.2% (LRG)	$1.09\times10^3~S~m^{-1}$ (LRG)	[32]
Wood	CO <sub>2</sub> pulsed laser 10.6 μm	_	<i>P</i> :1.6–8.6 W	<i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub> : 0.48 (LRG) C−C ≈ 75% (LRG)	10 $\Omega$ sq <sup>-1</sup> (LRG)	[98]

<sup>a)</sup>CW: Continuous wave; <sup>b)</sup>P: Power; <sup>c)</sup>W: Pulse width; <sup>d)</sup>F: Frequency; <sup>e)</sup>D: Energy density; <sup>f)</sup>PE: Pulse energy; <sup>g)</sup>Nd:YAG: Neodymium-doped yttrium aluminum garnet; <sup>h)</sup>E: Beam energy.





**Figure 6.** a) Schematic and photograph of LRG for supercapacitor. b) Photograph of an array of concentric circular patterns on GO film. c) SEM image of GO and LRG (scale bar, 100  $\mu$ m). d) Cyclability tests of the as-prepared sandwich and concentric circular devices. e) Histogram



as both an electrolyte and an electrode separator. The concentric circular patterns were fabricated on GO film, and the SEM image of LRG indicates long-range ordered structure induced by laser. The resulting devices demonstrate a high power density of 9.4 W cm<sup>-3</sup>. After 10 000 cycles, there is a 30–35% drop in the capacitance. To miniaturize the device and reduce production cost, Thekkekara et al. integrated LRG supercapacitors on the backside of the solar cell, which could lead to standalone photovoltaic systems.<sup>[112]</sup>

Owing to the intensive  $\pi$ - $\pi$  interaction of graphene, its sheets exhibit a strong tendency to restack together. The restacking propensity leads to a significant decrease of the ion-accessible surface area and thus low capacitance.<sup>[113]</sup> To prevent restacking, singlewalled carbon nanotubes (CNTs) with 1-2 nm diameter were introduced between the GO layers, as shown in Figure 6f.<sup>[30]</sup> Figure 6g,h shows the laser fabrication procedure of the supercapacitors and the photograph of the devices. Amiri et al. fabricated supercapacitors with the GO/ZnO mixture by laser irradiation.<sup>[114]</sup> Compared with the pristine GO-reduced device, a 12-fold improvement in the specific capacitance was achieved. In addition, Wang et al. reported producing GO foam using laser reduction.<sup>[31]</sup> The GO foam was fabricated from a GO suspension with a freeze-drying method and pressing process. Due to its unique structure and highly accessible surface area, the LRG foam exhibits excellent electrochemical performance as electrodes for supercapacitors.

#### 4.2. LRG for Sensor Development

Owing to the ease of microfabrication in devices in addition to the innate excellent properties of LRG, a number of sensors have been fabricated based on LRG, including  $NO_2$  gas sensor, humidity sensor, strain sensor, and pressure sensor. The gas-sensing mechanism of LRG is ascribed to the adsorption/desorption of gaseous molecules on the surface of LRG, which act as electron donors

comparison of area-based capacitance density with external electrolytes. Inset: volumetric energy density versus power density data of the corresponding devices. a–e) Reproduced with permission.<sup>[28]</sup> Copyright 2011, Nature Publishing Group. f) Schematic showing the formation of GO/CNTs hybrid powder. g) Schematic illustration of fabrication process for the flexible micro-supercapacitor. h) Photograph of laser-scribed microdevices. f–h) Reproduced with permission.<sup>[30]</sup> Copyright 2014, Elsevier.



or acceptors and thus change the resistance.<sup>[115,116]</sup> Strong et al. reported a graphenebased NO<sub>2</sub> gas sensor using a laser reduction process.<sup>[33]</sup> The **Figure 7**a–c depicts the LRG on a flexible substrate and its application for NO<sub>2</sub> detection. The sensor shows sensitive, reversible sensing for NO<sub>2</sub> with LRG serving as both the electrode and the sensor probe.

Sun et al. presented the fabrication of a humidity sensor by two-beam interference laser reduction and patterning of GO, as shown in Figure 7d–f.<sup>[34]</sup> The hierarchical nanostructures introduced by variable distribution of interference laser increase the exposal surface area of LRG and improve the sensing performance. The resistance of the devices decreased by two orders of magnitude while increasing the relative humidity from 11% to 95% at 25 °C. These humidity sensors also have fast and tunable response/ recovery time (3 s response time and 10 s recovery time).

Tian et al. reported flexible strain sensors that can be fabricated by reducing GO with a Light-Scribe DVD burner.<sup>[117]</sup> The gauge factor (GF) of the strain sensor can be adjusted from 0.11 to 9.49 by designing the geometry size of LRG. The piezoresistance effect of the sensor may be attributed to graphene film cracking upon force application. Luo et al. studied LRG for a flexible strain sensor and its potential applications for gesture registration and human-machine interactions as shown in Figure 8a-f.<sup>[32]</sup> Due to its flexibility and high sensitivity, the LRG-generated strain sensors demonstrated great potential for developing customized flexible electronics. Tian et al. reported a LRG with foam-like structure and its application for pressure sensing as indicated in Figure 8g,h, where two samples with LRG patterns perpendicular to each other formed a cross-bar structure by face-to-face contact.<sup>[35]</sup> The pressure sensor exhibited high sensitivity (0.96 kPa<sup>-1</sup>) in the pressure range of 0-50 kPa because of the large interspacing between graphene layers and the unique microstructure of the LRG.

#### 4.3. LRG for Field Effect Transistor

Compared with thermal- or chemical-reduced GO or mechanically exfoliated graphene, LRG has the advantage of flexible fabrication at a specifiable location. In addition, the laser reduction process could be conducted in the last device fabrication step without affecting other manufacture procedures of the device. Guo et al. reported the application of an FET





**Figure 7.** a) LRG-interdigitated electrodes on GO film using PET as substrate. b) Same interdigitated electrodes transferred onto polydimethylsiloxane. c) NO<sub>2</sub> detection using a patterned flexible set of interdigitated LRG electrodes. a–c) Reproduced with permission.<sup>[33]</sup> Copyright 2012, American Chemical Society. d) Schematic process of laser interference treatment. e) *I–V* curves of LRG sensor. The inset is a photograph of a typical LRG humidity sensor. f) Humidity hysteresis characteristic of the GO and LRG sensors. d–f) Reproduced with permission.<sup>[34]</sup> Copyright 2012, Elsevier.







**Figure 8.** a) Photograph of seven graphitic sensors (S1–S7) on a curve-shaped composite part. b) Comparison of the resistance change for sensor S4 and commercial strain gauge at different compression loading levels. c–f) LRG for flexible and wearable sensors in human machine interactions: c) finger gestures recognition, d) robotic control, e) tactile sensing, and f) heartbeat sensing. a–f) Reproduced with permission.<sup>[32]</sup> Copyright 2016, Elsevier. g) Top view SEM image of the LRG surface with foam-like structure in false color. h) Cross-bar device structure of the pressure sensor based on the foam-like LRG. Inset showing a flexible LRG pressure sensor in hand. g,h) Reproduced under the terms of the Creative Commons Attribution 4.0 International license.<sup>[35]</sup> Copyright 2015, the authors, published by Nature Publishing Group.

fabricated with LRG as shown in **Figure 9**a–e.<sup>[37]</sup> The bottomgate FETs were fabricated with LRG channel between source and drain Au electrodes. The bandgap of LRG was modulated from 2.4 to 0.9 eV by adjusting the power of the laser from 0 to 23 mW. An optimized on–off current ratio of 56 was achieved at room temperature, which indicates a hole mobility of 0.19 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The same group also demonstrated N-doping and the simultaneous reduction of GO film by a femtosecond laser in an NH<sub>3</sub> atmosphere.<sup>[118]</sup> The highest nitrogen concentration of 10.3% was achieved with a laser power of 10 mW. The N-doped LRG channel was fabricated between prepatterned electrodes for n-type FET device. This n-type FET shows an







**Figure 9.** a) Scheme of the bottom-gate GO FET. Optical microscopic images of b) parallel microlines with different width, c) sinusoid, and d) hexagon grid were patterned between source and drain electrodes as a channel. e) *I*–V curves of the above three channels with  $V_g = 0$ . a–e) Reproduced with permission.<sup>[37]</sup> Copyright 2012, American Chemical Society. f) Schematic illustration of the experimental procedures for LRG FETs. g) Output characteristics of the LRG FETs. Inset is the photograph of an LRG FETs' array on a flexible PET substrate. f,g) Reproduced with permission.<sup>[36]</sup> Copyright 2016, Institute of Electrical and Electronics Engineers.

on–off current ratio of 5 with an electron mobility of 0.38 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>. A combination of p-type and n-type LRG devices will facilitate the manufacture of complicated and multifunctional LRG devices in the future. Beside the LRG channel, He et al.

reported all LRG FETs including LRG source/drain electrode arrays, LRG gate electrodes, and an LRG channel as depicted in Figure 9f,g.<sup>[36]</sup> It shows an on–off current ratio of 2.04 with an estimated hole mobility of 0.27 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This device shows unique advantages in both facile fabrication and flexible integration of graphene-based microdevices.

## 4.4. LRG for Optical Applications

Gu and co-workers have reported the nonlinear absorption response and refractive index of a GO film under increased laser irradiance.<sup>[119]</sup> During the transition from GO to LRG, the third-order nonlinear responses can be tuned by adjusting the laser input fluence. This group also demonstrated a GO ultrathin (about 200 nm) flat lens based on laser reduction technology.<sup>[47]</sup> A flat lens was fabricated in GO film by writing sub-micrometer concentric rings with laser, converting GO film to LRG. Since the film thickness, the refractive index and the transmission/extinction coefficient of LRG are all tunable by adjusting the laser power, the flat lens can be designed for the modulation of both amplitude and phase. The flat lens demonstrates a focusing efficiency of 32% for a wavelength range from 400 to 1500 nm. Based on GO-poly(vinyl alcohol) composites, Gu and co-workers reported a refractive-index modulation of LRG on the order of  $10^{-2}$ - $10^{-1}$  by adjusting the laser power from 3 to 15 mW.[120] The same group demonstrated refractive-index-modulated LRG for recording and reconstruction of holograms as shown in Figure 10a-c.<sup>[40]</sup> The refractive-index modulation was recorded in the GO-polymers by finely adjusting the laser intensity on each pixel. A colorful object was reconstructed through the wavelength-multiplexed phase hologram recorded in GO polymers.

Using the high photoabsorption and thermal conductance of LRG, Evlashin et al. reported a bolometer based on laser reduced GO film.<sup>[121]</sup> The device measurement and its photoresponse are shown in Figure 10d–f. The temperature coefficient of resistance (TCR) of LRG is as low as 0.3% K<sup>-1</sup> at 300 K (TCR of silicon, 3% K<sup>-1</sup>). For several micrometer films, an absorption of more than 98% for visible light and 90% for IR was achieved.

The optical transparency of LRG is comparable to other chemically processed the graphene film,[122] but laser direct writing of LRG offers great advantage in device integration. Kymakis et al. presented the integration of LRG into organic photovoltaic device as the transparent electrodes.<sup>[74]</sup> The device integrated with LRG electrodes displayed a powerconversion efficiency (PCE) of 1.1% (LRG film with 70% transparency and a sheet resistance of 1.6 k $\Omega$  sg<sup>-1</sup>). Although displayed lower performance than traditional indium tin oxide (ITO) electrodes (90% transmittance, a sheet resistance of 15  $\Omega$  sq<sup>-1</sup>), the LRG has advantages in its facile process, cost-effectiveness, and compatibility with flexible devices. The same research group also improved the transmittance of the rGO from 20% to 85% by patterning the mesh on the surface of rGO films with the laser.<sup>[123]</sup> With optimum laser patterned rGO (59.1% transparency and a sheet resistance of 565  $\Omega$  sq<sup>-1</sup>) as transparent electrodes, the photovoltaic device demonstrated a PCE of 3.05%.





**Figure 10.** a) Schematic illustration of the optical digitalization of refractive-index/phase modulation using a single fs pulse. b) Scheme of wide-angle 3D images. c) Reconstruction of color objects through the wavelength-multiplexed phase hologram recorded in GO polymers. a–c) Reproduced under the terms of the Creative Commons Attribution 4.0 International license.<sup>[40]</sup> Copyright 2015, the authors, published by Nature Publishing Group. d) Schematic of the measurements of LRG for bolometer application. e,f) Characteristics of photo response at a voltage of 0.5 V, at different rates of switching on–off. d–f) Reproduced with permission.<sup>[121]</sup> Copyright 2016, American Chemical Society.

#### 4.5. Other Applications

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Besides the applications mentioned above, some other applications including cancer treatment, water purification, lithium-ion batteries, electrothermal heater, and thermal sound source have also been studied recently. For biological applications, Li et al. reported that under the irradiation of a femtosecond laser, the GO nanoparticles in solution demonstrated intensive appearance and instant collapse of microbubbling of water in microseconds, which facilitated the destruction of cancer cells.<sup>[124,125]</sup> This microcavitation effect is induced by the ultrafast reduction of GO (physical and chemical changes) by femtosecond laser. The localized reduction of GO indicated that the laser microsurgery of the malignant cell could be achieved without harm to adjacent normal cells and blood vessels. For environmental applications, Buccheri et al. investigated the antibacterial activity and toxicity of GO and LRG.<sup>[126]</sup> After being exposed to the LRG at a concentration of 20 mg L<sup>-1</sup>, the bacteria exhibit membrane damage, which may be correlated to the morphology and size of LRG.<sup>[127]</sup> The LRG solution displays neither mortality nor sublethal effects in a fish embryo toxicity test on zebrafish at concentration eight times higher than 20 mg L<sup>-1</sup>. The combination of antibacterial and nontoxic functions of LRG is a promising option for water purification applications.

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Considering the porous structure of LRG yielded in the reduction process, laser-reduced free-standing graphene paper was studied as an anode for lithium-ion batteries.<sup>[107]</sup> This structure provides better electrolyte access to the electrode and enhances the lithium intercalation kinetics. Taking advantage of its effective electrothermal conversion, a flexible heater was fabricated based on LRG as shown in Figure 11a,b.<sup>[128]</sup> This LRG heater exhibits faster response time (23.3 °C s<sup>-1</sup>) than the conventional nichrome heater (<1 °C s<sup>-1</sup>) due to its high electrothermal performance. Its saturated temperature and heating rate can be improved greatly through repeated radiation. Based on LRG, Tao et al. presented a flexible 360° thermal sound source and its fabrication process is shown in Figure 11c.<sup>[129]</sup> The LRG strip was attached to the surface of a cylindrical bottle so that it can emit sound in a 360° direction. This 360° sound source exhibits omnidirectional directivity at frequencies of 10 and 20 kHz.

# 5. Conclusion

Laser direct writing of graphene has distinctive features of (1) Highly localized reductionunlike the conventional thermal/chemical reduction, laser irradiation selectively reduces the GO or polymer film and creates desired micropatterns with accurate spatial control; (2) sub-micrometer feature size-the laser written spots/lines currently can be down to several hundred nanometers wide with much room for further improvement; (3) multifunctional LRG material-as discussed above, the LRG exhibits tunable conductivity, porous graphene structure, adjustable refractive index, and film thickness; (4) unsurpassed flexibility in pattern designs, substrate choice, device integration, and GO reduction tunability; (5) environmentally friendly-the process requires neither large-scale hightemperature environments nor reactive chemicals. Laser direct writing of graphene

offers a technology with significant application potential for supercapacitors, sensors, optical devices, displays, and nanoand microcircuits, as demonstrated by various studies.

For the future, LRG with better performance including higher conductivity and smaller feature size, and broader applications are anticipated. Several aspects deserve particular attention: (1) the precursor material—direct conversion of polymer into graphene offers a revolutionary opportunity for flexible electronics, therefore, it is highly desirable to explore

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LRGO with aligned direction

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silver paste

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laser

LRGO

copper tape

LRGO with aligned direction

vertical to the current

**Figure 11.** a) The preparing process of LRG. b) The LRG-based heaters with different aligned directions. a,b) Reproduced with permission.<sup>[128]</sup> Copyright 2016, American Institute of Physics Publishing limited liability company. c) Fabrication process of the 360° thermal sound source. Reproduced under the terms of the Creative Commons Attribution license.<sup>[129]</sup> Copyright 2016, the authors, published by MDPI.

the possibility of turning polymers other than PI to graphene directly through polymer design and laser adjustment. Direct conversion from biomass, such as wood and crop residues, is also highly interesting for providing an additional value-adding solution to waste. (2) the lasers—new lasers combined with advanced microscopy, for example, extremely small laser spots through stimulated emission depletion microscopy<sup>[130]</sup> and/ or improved flexibility in wavelength and power tuning, can be employed to enhance the properties of LRG. (3) The reduction process—like most other reduction methods,<sup>[131–136]</sup> it is

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difficult to remove all the oxygen functional groups. The laser reduction process can only restore part of the hexagonal sp<sup>2</sup> carbon network. The fundamental study on the mechanism of the laser reduction process requires more attention for optimization. In addition, a combined reduction process may offer an effective route to enhance the reduction quality.

Toward applications and device fabrications, the technology of laser direct writing of graphene offers tremendous opportunities. Here we highlight two areas that are of particular interest: (1) with the increasing tunability we are gaining on LRG properties, we envision that the very same technology can be employed to write different components of a device, such as electrodes, sensor probes, transistors, conductive tracks, optical parts, antenna, and energy storage units, all on one chip. 2) Combined with a 3D-printing platform, LRG technology can produce embedded devices with 3D architectures for self-monitoring and communication, as well as mechanical property improvement. Overall, laser direct writing of graphene has significant potential to be adopted in various real-world applications.

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