Tuning the sub-processes in laser reduction of graphene oxide by adjusting the power and scanning speed of laser

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Abstract

Laser reduction of graphene oxide is a promising technology for manufacturing advanced devices such as supercapacitors, sensors and transistors, owing to its distinctive advantages in selective and localized GO reduction, direct micro- nanoscale patterning, and no requirement for chemicals. However, the fundamental mechanism underlying the laser induced reduction is still not well understood. In this paper, we demonstrate that by adjusting the power and scanning speed of a 780 nm femtosecond laser, not only can one distinguish, but also effectively tune, two coexisting sub-processes during the laser reduction, namely the direct conversion from sp^3 to sp^2

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carbon and removal of oxygen functional groups. Different oxygen containing groups demonstrate varied degrees of reduction when the power of the laser was varied. Our study provides solid and direct evidence for the coexistence of two sub-processes in the laser induced reduction of graphene oxide, which is essential for both mechanistic understanding and practical adoption of this technique in real word applications.

1. Introduction

Graphene has become one of the major interesting research subjects following its discovery in 2004 [1, 2] due to its high electrical and thermal conductivities, optical transparency, and exceptional mechanical strength, making it a promising candidate for many applications including transparent electrodes [3], capacitors [4], sensors [5] transistors and memory devices [6]. Different preparation methods of graphene have been studied extensively, with the most popular ones being mechanical exfoliation [7], epitaxial growth [8], chemical vapor deposition (CVD) [9, 10] and the reduction of graphene oxide (GO) [11]. As a mainstream precursor for reduced graphene, GO has a single- or multilayer atomic structure which consists of carbon skeletons bearing a resemblance to graphene but being decorated with oxygen containing groups and defects. GO can be partially converted into graphene sheets by removing its oxygen-containing groups via thermal [12], chemical [13], microwave [14], plasma [15], photo [16-19], or laser reduction [20-25]. Compared to other methods, GO reduction has great potential for mass production of graphene since GO can be produced from graphite on a large scale with

cost-effective chemical methods [26]. Moreover, it can naturally form stable aqueous colloids due to its high hydrophilicity [27], which is a desirable property for applications that require solution processing.

Compared to the thermal, chemical or plasma reduction of GO, the laser reduction method demonstrates several unique advantages, including selective and localized treatment, sub-micron feature size (down to several hundred nanometers [28]), no requirement for chemicals or heating equipment, and convenient and flexible patterning compatibility [29]. Therefore, laser reduction of GO thin film is ideal in several applications including supercapacitors [30-32], sensors [33-35], and field transistors [36], whereby reduction and device patterning can be achieved simultaneously. Lasers with various wavelengths (248 nm [37], 800 nm [38], 10.6 μm [39]) and different pulse durations (continuous wave, nanosecond [40], picosecond [41], femtosecond (fs) [42]) have been used to perform the reduction. Kaner's group demonstrated a scalable fabrication of supercapacitors by laser direct-writing on GO films and more than 100 micro-supercapacitors were produced in less than 30 minutes [43], illustrating an enormous potential for roll-to-roll production.

However, so far the fundamental mechanism of laser reduction of GO is not yet fully understood, which is essential to tune and optimize the properties of laser reduced graphene oxide (LRGO) for real applications. In limited reports on the mechanism of laser reduction investigated by a few research groups [28, 40, 44, 45], the proposed mechanisms could be divided into three categories: sole photothermal driven conversions [44], sole photochemical driven conversions [28] and coexistent photothermal- and photochemical driven conversions [40,

45]. In the photothermal theory, the laser reduction of GO results from the thermal effects induced by the laser, namely, the oxygen functional groups are removed because of localized high temperatures. In the photochemical theory, the laser reduction of GO is attributed to a direct breakage of the chemical bonds between the carbon and oxygen atoms (such as C–O or C=O) resulting in the removal of the oxygen. A recent report from Arul et al. proposed that the reduction takes place in two processes, namely the photochemical removal of oxygen by photochemical process, and the photothermal conversion of reduced carbon into sp^2 graphene structure [40]. Nevertheless, it is difficult to accurately and directly prove whether the temperature induced by the laser is higher than the thresholds for initiating the reduction of GO. Considering the possible multiphoton absorption in the process, the threshold of laser wavelength for photochemical effect is also ambiguous. Moreover, the involvement of the photochemical and photothermal effects in the oxygen removal and conversion of sp^3 carbon into sp^2 carbon is still unclear. Detailed study of the reduction effects on different oxygen containing groups is absent. Therefore, a systematic study is needed for connecting the dots to provide a better understanding of the overall process.

This study provides a systematic investigation on the mechanism of laser reduction. The GO film is reduced by a femtosecond (fs) laser (780 nm wavelength; 70 fs pulse width; 50 MHz repetition rate) with different laser power and scanning speeds. After the laser treatment, optical microscopy, surface profiling, scanning electron microscopy (SEM), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) were employed for characterizing the carbon structures. Our results confirm that the reduction process consists of two adjustable

fundamental sub-processes depending on laser power and scanning speed: the conversion of sp^3 carbon to sp^2 carbon and the removal of oxygen functional groups. At lower power of 3 mW (fluence 1.9 mJ cm^{-2}), there is clear conversion of sp^3 carbon (20.99%) to sp^2 carbon, while the percentage of oxygen containing groups only decreases by 5.17%. Increasing the laser power up to 13 mW (fluence 8.3 mJ cm^{-2}), we observe a reduction in oxygen containing groups of 13.28%, together with the distinctive conversion of sp^3 carbon to sp^2 carbon, indicating a dependence of these two sub-processes on the laser power. Furthermore, different oxygen containing groups demonstrate varied degree of reduction for the same laser power. An obvious decrease in the percentage of C=O is noticed at a laser power of 3 mW, while that of C–O is not observed until the laser power reaches to 13 mW. The COOH group does not show a distinctive decrease with laser power from 3 to 13 mW. We also demonstrate that the degree of reduction, the decrease of thickness of LRGO and the conductivity of LRGO can be modulated by adjusting the laser power and its scanning speed. These findings provide a better understanding of the fundamental mechanism underpinning laser reduction as well as an insight to how to effectively tune the properties of LRGO.

2. Experiment

2.1 Method

GO was synthesized with modified Hummers method [46]. The glass wafer was cleaned with acetone, ethanol and then pure water with the aid of ultrasound. After cleaning, the glass

was treated with Piranha solution (7:3 98% H_2SO_4 :30% H_2O_2) and dried at 60 °C in air before use. The GO dispersed in water at a concentration of 2.4 g/L was spin-coated at 1000 rpm for 1 minute on the glass wafer, dried at 60 °C and the process was repeated 4 times. The thickness of GO film is 110 nm. A fs pulse laser with 780 nm center wavelength (70 fs pulse width, 50 MHz repetition rate, spot size of 2 μm diameter) was employed for GO reduction. The laser power was adjusted from 3 to 13 mW (equivalent laser fluence ranging from 1.9 to 8.3 mJ cm^{-2}). The source laser is a custom-made erbium-doped fiber cavity laser. The laser is focused with a Newport M-40X objective lens with effective focal length of 4.5 mm. The micromachining stage is the Newport laser uFAB microfabrication workstation. The laser treatment on GO film is carried out in ambient conditions.

The samples for conductivity test were fabricated with the following procedures: the GO film was spin-coated on glass wafer. The gold electrodes were sputtered on the top of the GO film with a gap of about 600 μm . Subsequently, a LRGO wire was laser-written to connect the two electrodes.

2.2 Characterizations

Raman spectra were acquired with Raman Spectrometer Renishaw Invia (using 514 nm excitation wavelength and a 50 $\times$ objective, acquisition parameters: 0.05 mW power, 10 s exposure time, 1 accumulation, and 2400 l/m gridding). Peak fitting of the Raman data was carried out using the WiRE3.3 software. X-ray photoelectron spectroscopy (XPS) was performed with Kratos Axis ULTRA X-ray Photoelectron Spectrometer. The peak fitting of the XPS data

was carried out using the CasaXPS software. The XRD data were collected with Rigaku SmartLab with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The optical micrographs were obtained with a microscope from ProSciTech, camera UCMOS05100KPA. The SEM images were acquired with JEOL JSM-7001F. The thickness of the films was measured with Dektak 150 surface profiler. The film resistance was measured with a two-probe tester, Model 6430 source meter (Keithley Instruments Inc., USA).

3. Results and discussion

The schematic in Figure 1(a) illustrates a fs pulsed laser with central wavelength at 780 nm is employed to reduce the GO film (thickness approximately 110 nm) fabricated on glass substrate. For studying the effects of laser power and scanning speed, an array of LRGO rectangle spots have been directly written by the laser irradiation to allow a systematic study. The inset shows an optical microscopic image of LRGO array, demonstrating that these LRGO rectangles treated with various power of laser and scanning speed show varied optical contrast, which may result from different reduction degrees by the laser [47]. The SEM image in Figure 1(b) shows that the laser scanned area is brighter due to the abundant emission of secondary electrons [48]. The optical image displayed as an inset in Figure 1(b) shows the laser scribed Griffith University logo, illustrating the flexibility of this technique in pattern creation. The smallest feature size of LRGO with the employed laser is about 2 μm in diameter. As shown, the laser writing technology is highly flexible and straightforward for patterning, very applicable for micro-device

fabrication. The magnified SEM images of GO and LRGO displayed in Figure 1(c) show that there is no discernible modification on the morphology of film after the laser treatment.

Figure 1 (a) Schematic figure of laser reduction of GO film. The inset shows the microscopic image of GO treated with varied power of laser and scanning speed, scale bar 100 μm . (b) The SEM images of the GO treated with laser, scale bar 10 μm . The inset shows Griffith University logo under microscopy, scale bar 100 μm . (c) The enlarged SEM image of GO and LRGO, scale bar 1 μm .

3.1 The influence of fs laser parameters on the degree of reduction

To understand the influence of the fs laser parameters on the extent of the GO reduction, XPS and Raman spectroscopy were performed to understand the carbon bonding structure and the change in oxygen quantity and chemical composition. Figure S2 displays the survey XPS of GO and LRGOs fabricated with various laser powers (3 mW, 5 mW, 7.5 mW, 10 mW, 13 mW) at

scanning speed of 5 $\mu\text{m/s}$, showing the presence of carbon and oxygen atoms. With increased laser power, it is observed that the intensity of C1s peak is significantly increased, while that of the O1s peak decreased, indicating a loss of oxygen atoms. The atomic carbon to oxygen ratios (C/O) was calculated based on the area of the peaks of C1s and O1s spectra. **Figure 2(a)** shows the dependence of C/O on laser power; There is a clear trend of increasing C/O from 2.46 (GO) to 3.35 (LRGO 13mW) with the increased laser power, which illustrates that the amount of oxygen functional groups in LRGO can be adjusted by the laser power.

A closer inspection on the acquired XPS and Raman spectra revealed more details on the defects and structure of the LRGOs. The Raman spectra of LRGO samples fabricated with various laser power (from 3 to 13 mW) and laser scanning speed (from 0.1 to 5 $\mu\text{m/s}$) were acquired. Figure 2(b) presents the Raman spectra of GO and LRGO (7.5 mW, 0.2 $\mu\text{m/s}$) with their fitting lines, including D, G and N (non-crystallized sp^2) bands. The D-band (1355 cm^{-1}) results from defects in the plane structure of graphite due to the presence of oxygen containing groups, while the G-band (1604 cm^{-1}) is attributed to an E_{2g} mode of graphite associated with the stretching motion of sp^2 carbon atoms [49, 50]. Both D and G bands originate from different vibrational modes of graphitic structures, while the N band (1540 cm^{-1}) is due to the amorphous sp^2 carbon. The shape of those peaks depends on the crystallite size; when the crystallites become larger, the peaks become narrower [51, 52]. The band intensity ratio I_D/I_G reflects the degree of disorder in the graphene-structure [53]. As shown in Table S2, the crystalline size in the axis (L_a) can be obtained from I_D/I_G using the equation [54]:

$$L_a(\text{nm}) = (2.4 \times 10^{-10}) \times \lambda_i^4 \times \left(\frac{I_D}{I_G}\right)^{-1}$$

where λ_l is the wavelength of the Raman laser ($\lambda_l = 514 \text{ nm}$).

Figure S3(a) shows the Raman spectra of GO and LRGOs fabricated at laser scanning speed from 0.1 to 5 $\mu\text{m/s}$ with constant laser power of 5 mW. At the laser power of 5 mW, a decrease of the I_D/I_G ratio can be observed with a decrease in the scanning speed. Figure S3(b) displays the Raman spectra of GO and LRGOs fabricated at laser scanning speed of 0.2 $\mu\text{m/s}$ with laser power increased from 3 to 13 mW, which shows a consistent decrease of the I_D/I_G ratio with the increase of the laser power. This decrease of I_D/I_G illustrates a successful reduction of GO, resulting in fewer defects and larger crystalline size. Figure S3(c-d) show the Raman spectra of LRGO (13mW, 0.2 $\mu\text{m/s}$) with 10 accumulations (c) and 30 accumulations (d). The 2D Raman band (2700 cm^{-1}) is the second order of zone-boundary phonons [55]. Both graphene and graphite demonstrate strong 2D peak, while graphene oxide does not feature such an obvious 2D peak. After the 780 nm fs laser treatment of the GO, the 2D band did not appear, which suggests that the fs laser reduction is localized and does not develop large planar sheet of graphene. More comprehensive results of the I_D/I_G dependence on laser power and scanning speed are shown in Figure 2(c) and Table S3. Five spots of each LRGO sample were measured with small variation of I_D/I_G , illustrating its good consistency and uniform. After laser reduction, the I_D/I_G ratio decreased from 1.37 (for GO) to 1.13 (for LRGO 13 mW, 0.1 $\mu\text{m/s}$). Figure 2(c) demonstrates the tendency that higher laser power combined with lower scanning speed results in a reduced I_D/I_G value, which illustrates the adjustable defects density and structure of LRGO.

Figure 2(d) shows the I_D/I_G versus energy density (laser energy density = laser power/(scanning speed $\times$ track width)) at different laser power. It can be noticed that at a constant laser power, with

an increase in the laser energy density, namely slower scanning speed, the value of I_D/I_G decreases until it becomes saturated. With the increase of the laser power, the I_D/I_G value saturates at relatively lower energy density and reaches a lower value. It can be concluded that the laser power (fluence) plays a decisive role on the I_D/I_G change, while the energy density can also affect it to some extent. The results correlated with energy density provides a more general guidance to modulate the properties of LRGO by changing the parameters of the laser. It is worth noting that since GO can be reduced even under ambient conditions due to long exposure to room light [56], the contrast between the laser-reduced areas and the un-reduced areas of a GO film could decrease. For its stability and reliability in applications, the GO treated with laser should be encapsulated with protection to avoid the further reduction.

Figure 2 (a) The C/O ratio of GO and LRGOs fabricated with laser power of 3 mW, 5 mW, 7.5 mW, 10 mW and 13 mW. (b) The Raman spectra of GO and LRGO (7.5 mW, 0.2 $\mu\text{m/s}$) and the fitted curve. (c) The dependence of I_D/I_G of LRGO on laser power and laser scanning speed. (d) The dependence of I_D/I_G on energy density and laser power.

3.2 The modulation of the thickness of laser reduced graphene oxide

After irradiation, the film thickness was measured with surface profiler and the dependence of decreased thickness on energy density calculated from the laser power (3-13 mW) and laser scanning speed (0.1, 0.2 and 0.5 $\mu\text{m/s}$) is shown in Figure 3. The inset of **Figure 3** shows the schematic of the cross section of GO film during laser irradiation. The thickness of LRGO decreases with increased laser energy density but saturates at the energy density of 37.5 $\text{mJ } \mu\text{m}^{-2}$. The thickness decrease can be adjusted from 20% (22 nm) to 70% (77 nm) of its original thickness, namely 110 nm, by modulating the laser energy density. This reduction of thickness likely results from the mass loss from the GO film and the laser induced ablation [38]. For relatively high scanning speed ($> 1 \mu\text{m/s}$), the thickness decrease is indistinguishable by the Surface Profiler. This suggests that when the laser energy density is high (scanning speed is low), there may be higher thermal effect, which results in laser ablation effect. In terms of technology capability, this result demonstrates that in addition to 2-dimensional (2D) patterning, the laser reduction can also simultaneously introduce 3 dimensional (3D) features that are adjustable by the laser parameters.

Figure 3 The dependence of thickness decrease on the laser energy density, the inset is the schematic depicting the cross section of a GO film under laser treatment.

3.3 The conductivity of laser reduced graphene oxide

After irradiation, the conductivity of the LRGO is improved compared to that of GO. The laser power was kept at 5 mW with scanning speed varied from 0.1 to 5 μm/s. **Figure 4** displays the dependence of conductivity on laser energy density. The inset shows schematic figure of conductivity test (left) and the microscopic image of a LRGO line between two Au electrodes for the conductivity test (right). Before laser treatment, the conductivity of GO is about 10^{-3} S/m. After laser reduction, the conductivity of LRGO was improved to 45.5 S/m under scanning speed of 0.1 μm/s, that is 4 orders of magnitude greater than that of GO. With different laser scanning speeds, the conductivity of LRGO varies from 19 to 45.5 S/m.

It's worth noting that the conductivity of LRGO in the various reports [30, 53, 57, 58] ranged from 10^1 to 10^4 S/m, with the highest reported value of 2.56×10^4 S/m [50]. One reason

for this high variation of the LRGO conductivity could be the different qualities of the starting GO, which shows conductivities ranging from 10^{-4} to 10^1 S/m [41, 57, 59]. During GO film fabrication, GO flakes stack and the resistance between stacked layers plays a significant role in the overall film resistance [60]. The other reason could be the different reduction degree of GO. Strong et al. demonstrated high reduction degree with a high C/O ratio at 27.8, enhancing the conductivity from 6.6×10^{-3} S/m (GO) to 1.65×10^3 S/m (LRGO) [34]. Since the conductivity of GO typically varies from 5×10^{-4} and 4×10^{-1} S/m [61, 62] and the conductivity measurement is subject to the specific setup, quality of contacts, sample preparation etc., it would be inaccurate to compare the conductivities between different studies. Rather, it is the conductivity difference between pre and post-treatment materials that matters [29].

Figure 4 The dependence of the LRGO conductivity on laser energy density. The inset shows the

schematic figure of conductivity test (left) and microscopic image of a LRGO line between two gold electrodes for conductivity test, the scale bar is 100 μm (right).

3.4 The mechanism of fs laser reduction

We further investigated the mechanism of fs laser reduction. Different laser power was used to tune the reduction degree of GO at scanning speed of 5 $\mu\text{m/s}$. The C1s spectra of GO and LRGOs are deconvoluted into several main peaks including: sp^2 hybridized carbon (C–C sp^2 284.5 eV), sp^3 hybridized carbon (C–C sp^3 285 eV), epoxide/hydroxyl (C–O 286.6 eV), carbonyl (C=O 287.6 eV), and carboxyl (COOH 288.6 eV). Table S4 provides the atomic concentration percentage of chemical state components of GO and LRGOs in the XPS spectra. The CC refers to the sum of C–C sp^2 and C–C sp^3 , and the CO is the combination of C–O, C=O and COOH. The ratio of percentage of CC bond to CO bond rises from 1.02 (GO) to 1.76 (LRGO 13 mW), which reveals the effective removal of oxygen after laser treatment.

Figure 5(a-b) illustrates the dependence of atomic concentration percentage of chemical components on laser power. Three main stages can be observed with the increase of laser power. At the first stage (laser power 3 mW), the restoration of C–C sp^3 to C–C sp^2 is obvious with a decrease of 20.99% in the percentage of C–C sp^3 and increase of 26.16% in that of C–C sp^2 . The percentage of CO decreased 5.17%, which mostly results from the decreased percentage of C=O. At the second stage (laser power from 5 to 10 mW), both the percentage of CO and the percentage of C–C sp^2 are relatively stable, compared to those of the first stage. There is no obvious tendency of further oxygen removal with a laser power of 10 mW. In the third stage (laser power 13 mW), there is a clear further 8.11% decrease of the percentage of CO compared to that of the first stage. In the reduction process, two important sub-processes can be concluded: the restoration of sp^3 to sp^2 and the removal of oxygen, and these two sub-processes can be tuned by adjusting the laser power.

Figure 5(c-f) shows the photoemission spectra of the C1s of GO and LRGOs fabricated with different laser powers and their curve-fits. The XPS spectra of LRGOs fabricated at different

laser scanning speed with the power of 7.5 mW are shown in Figure S5. The laser scanning speed also demonstrates the modulation over the reduction of different oxygen components. Table S6 illustrates the percentage of chemical components with different scanning speeds. It can be concluded that the percentage of oxygen functional groups and CC/CO ratio can also be adjusted by changing the laser scanning speed.

Figure 5 (a-b) The dependence of atomic concentration percentage of chemical components on laser

power. (c-f) Peak fitted C1s XPS spectra of (c)GO, and LRGOs fabricated at (d) 3 mW (e) 7.5 mW (f) 13 mW.

Figure 6(a) shows the XRD patterns of GO and LRGOs fabricated under different laser powers at scanning speed of 5 $\mu\text{m/s}$, exhibiting a typical peak around 11.92° (002'). Bragg's equation was applied to evaluate the distance between layers, denoted as D (Figure 6(b) and Table S5). It is found that after the fs laser treatment of GO, the inter-layer distance has expanded from 7.44 (GO) to 7.75 Å (LRGO 13 mW), as shown in Figure 6(c). This expansion of interlayer space could result from the rapid thermal evaporation of intercalated materials, such as sulfuric acid [63] and water molecules [64], which indicates the thermal effect of the laser.

Figure 6 (a) XRD analysis of GO and LRGOs with different laser powers at scanning speed of 5 $\mu\text{m/s}$. (b)

The dependence of layer distance on the power of laser. (c) Schematic illustration of the enlarged layer

distance after laser reduction of GO film

3.4.1 The restoration of sp^3 to sp^2

Figure 7 demonstrates the dependence of the sp^3 to sp^2 conversion and oxygen removal on the power of laser. The conversion of sp^3 carbon into sp^2 carbon is very distinctive (20.99%) at the laser power of 3 mW and remains at similar level when the laser power is increased to 13 mW. After irradiation with 3 mW laser, the ratio of C–C sp^2 to C–C sp^3 raises significantly from 0.87 to 8.14. Before laser treatment, the GO sample had 23.44% C–C sp^2 and 27.09% C–C sp^3 . After

laser reduction at 3 mW, the percentage of C–C sp^3 decreased from 27.09% to 6.09%, while the percentage of C–C sp^2 increases from 23.44% to 49.60%. This restoration process reorganized defective structure in GO back to graphene structure. Meanwhile, the percentage of CO (oxygen containing groups) only decreased 5.17% during this process. Our results show that the restoration of C–C sp^3 to C–C sp^2 can occur at relatively low power without having much oxygen removed. Direct conversion of sp^3 to sp^2 carbon has been reported both experimentally and theoretically [65–67]. The activation energy for this conversion was determined to be 3.5 ± 0.9 eV or 3.3 eV [65, 66] and this conversion process can be triggered by thermal or photo treatment [65, 67]. Table 1 lists the comparison of sp^2/sp^3 and CC/CO of GO reduced with different methods. This laser reduction methods shows a high sp^2/sp^3 of 12.18.

3.4.2 The removal of oxygen during reduction

By increasing the fs laser power to 13 mW, the percentage of CO decreased from 49.47% (GO) to 36.19% (LRGO 13 mW), indicating a substantial oxygen removal. However, the laser reduction process demonstrates varied degrees of effect on different oxygen-containing groups. There is an obvious decrease of the percentage of C=O, when the laser power is 3 mW or above. While the percentage of C–O does not decrease substantially until the laser power reaches 13 mW. For the percentage of COOH, there is no distinctive change after applying laser power from 3 to 13 mW.

Our finding revealed that the 780 nm fs laser reduction exhibits both carbon atom restoration and the removal of oxygen. At a lower laser power (3 mW), the restoration takes the main effect and there is little oxygen removal during the reduction. At a higher power (13 mW), further oxygen removal become more obvious. Although the fs laser is considered to be ineffective for generating heat because of its ultra-short duration [68], due to the recombination of electrons and holes, heating is also accompanied with the photochemical process [45]. The fs laser can still produce considerable thermal for GO reduction processes and might also cause the thermal

ablation and thermal expansion of LRGO interlayers. The temperature under such a laser system's irradiation has been estimated to be 304 °C (3 mW) and 340 °C (13 mW), employing the model developed by Li et. al [47]. It's been established that the threshold temperature for reducing GO is in the range of 200-230 °C [69, 70] and the higher the temperature above this point the increased reduction extent can be achieved [71]. Therefore, when our laser power varies from 3 mW to 13 mW, the elevated temperatures can all result in GO thermal reduction. With increased laser power, the temperature induced by the laser also increases, enhancing the removal of oxygen components. Moreover, considering that the threshold of GO photoreduction is at about 390 nm [72], two-photon absorption is likely to occur, which induces the photochemical effect that can play an important role in the reduction process. It can be concluded that both the photochemical and photothermal effects induced by the 780 nm fs laser might coexist in the restoration and oxygen removal processes.

Figure 7 The dependance of the conversion of sp^3 to sp^2 and the removal of oxygen on laser power.

Table 1 The comparison of components of GO reduced with different methods

Reduction methods of GO	sp^2/sp^3	CC/CO	Refer.
Chemical reduction	1.28-3.29	1.37-2.24	[73]
Hydrothermal reduction	5.58-6.6	3.45-4.16	[74]
Thermal reduction	-	3.44	[75]
Laser reduction	6.62-12.18	1.19-1.76	this work

4. Conclusions

In conclusion, we have studied the influence of laser fluence (power) and energy density (power, scanning speed) of a 780 nm fs laser in reducing the GO film. Our results confirm that there are two sub-processes in the laser reduction process, namely the direct conversion of sp^3 carbon into sp^2 carbon and the removal of oxygen. Both the photochemical and photothermal effects appear to be involved in the sub-processes of the removal of oxygen and the conversion of sp^3 to sp^2 .

Importantly, we found that the two coexisting sub-processes during the laser reduction can be tuned by adjusting the power and scanning speed of the laser. The conversion of sp^3 hybridized carbon into sp^2 carbon is very distinctive (20.99%) at low laser power of 3 mW and remains stable at about 21% with increasing the power of laser to 13 mW. In contrast, the removal of oxygen is limited (about 5%) until the laser power is raised up to 13 mW. At the power of 13 mW, the removal of oxygen can be enhanced to 13.28%.

We have also found that the amount of the different oxygen-contained groups can be controlled by the power of laser. The percentage of C=O decreased obviously from 9.98% to 4.32% when the laser power was only 3 mW, but the percentage of C–O did not decrease substantially until the laser power reaches 13 mW. It's also noted that the percentage of COOH (about 4%) remained almost constant despite the change in laser power in the range of 3 to 13 mW.

This selective and controllable reduction of GO could be utilized to prepare LRGO with precisely controlled functional groups for specific applications. The C-O groups attached to the basal planes are the main influencing factor on the conductivity of reduced GO while C=O present at the edges have a limited influence. Consequently, by selectively eliminating the C-O groups and preserving the C=O groups, the RGO demonstrates improved electrical conductivity and still be dispersible in solution [11, 76]. By adjusting laser fluence (power), the content of oxygen containing groups of the LRGO can be decreased from 49.47% to 36.19%; the I_D/I_G ratio of LRGO can be modulated from 1.40 to 1.13; and the decrease of film thickness during the laser induced reduction can be varied from 20% to 70% of the original thickness of GO film. The optimum condition for reducing GO using I_D/I_G ratio as the indicator is the fluence of 8.3 mJ cm⁻² and energy density of 65 mJ μm⁻² (power 13 mW, scanning speed 0.1 μm/s) in our laser system. After laser reduction, the conductivity of GO can be improved from 10⁻³ S/m to 45.5 S/m. This research provides solid evidence for the dual sub-processes underlying the laser induced reduction of GO, which is critical for mechanistic understanding as well as the effective modulation of LRGO for real applications. Given the current scale of GO production and its broad applications in energy storage, electronics, and catalysis etc., such a laser-induced direct reduction method can be envisioned as a facile process that can be readily incorporated into in line reduction of GO in a roll-to-roll process.

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Supplementary information

Table S1 the parameters of the laser used in the experiment

Center Wavelength	780 nm
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Pulse width	70 fs
Repetition rate	50 MHz
Max. laser power	13 mW
Laser spot	2 μm

Table S2 the crystal length versus laser power and laser scanning speed

La(nm)	5	2	1	0.5	0.2	0.1
(standard	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$
error)						
	11.97	12.27	12.43	12.97	12.94	13.16
3 mW	(0.15)	(0.17)	(0.07)	(0.10)	(0.05)	(0.11)
	12.27	12.85	12.96	13.17	13.71	13.77
5 mW	(0.20)	(0.08)	(0.15)	(0.10)	(0.05)	(0.09)
	12.69	13.57	13.83	13.93	14.09	14.23
7.5 mW	(0.05)	(0.10)	(0.03)	(0.08)	(0.02)	(0.10)
	12.99	13.58	14.12	14.09	14.46	14.37
10 mW	(0.05)	(0.10)	(0.11)	(0.09)	(0.11)	(0.14)
	14.51	14.47	14.66	14.70	14.66	14.86
13 mW	(0.06)	(0.08)	(0.08)	(0.26)	(0.09)	(0.10)

Table S3 the Raman I_D/I_G ratio of LRGO versus laser power and laser scanning speed

I_D/I_G	5	2	1	0.5	0.2	0.1
(standard error)	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$	$\mu\text{m/s}$
	1.40	1.37	1.35	1.30	1.29	1.28
3 mW	(0.018)	(0.02)	(0.008)	(0.005)	(0.009)	(0.01)
	1.37	1.30	1.29	1.27	1.22	1.22
5 mW	(0.022)	(0.008)	(0.014)	(0.01)	(0.005)	(0.008)
	1.32	1.23	1.21	1.20	1.19	1.18
7.5 mW	(0.005)	(0.009)	(0.003)	(0.007)	(0.002)	(0.008)
	1.29	1.23	1.19	1.19	1.16	1.17
10 mW	(0.005)	(0.009)	(0.009)	(0.008)	(0.008)	(0.011)
	1.15	1.16	1.15	1.14	1.15	1.13
13 mW	(0.005)	(0.006)	(0.007)	(0.022)	(0.007)	(0.009)

Table S4 XPS chemical state components of GO and LRGOs with different laser power

Sample	C-C sp^2 284.5 eV	C-C sp^3 285 eV (± 0.2)	C-O 286.6 eV (± 0.2)	C=O 287.6 eV (± 0.2)	COOH 288.6 eV (± 0.2)	CC C-C sp^2 + C-C sp^3	CO C-O+C =O+CO OH	CC / CO
GO	23.44%	27.09%	34.78%	9.98%	4.72%	50.53%	49.47%	1.02
LRGO-3 mW	49.60%	6.09%	36.38%	4.32%	3.61%	55.69%	44.31%	1.26
LRGO-5 mW	47.12%	7.12%	36.32%	5.40%	4.04%	54.24%	45.76%	1.19

LRGO-7 .5 mW	52.94%	5.06%	33.80%	4.00%	4.20%	58.00%	42.00%	1.38
LRGO-1 0 mW	51.80%	4.25%	34.73%	5.25%	3.96%	56.05%	43.95%	1.28
LRGO-1 3 mW	58.23%	5.57%	26.57%	5.18%	4.45%	63.81%	36.19%	1.76

Table S5 layer distance and crystalline size based on XRD

Sample	(002')	
	Position (2 θ)	Layer distance (Å)
GO	11.92	7.43
LRGO-3 mW	11.4	7.77
LRGO-5 mW	11.25	7.87
LRGO-7.5 mW	11.49	7.71
LRGO-10 mW	11.35	7.81
LRGO-13 mW	11.23	7.89

Table S6 XPS chemical state components of GO and LRGOs with different scan speed

Sample	C-C sp ² 284.5 eV	C-C sp ³ 285 eV (±0.2)	C-O 286.6 eV (±0.2)	C=O 287.6 eV (±0.2)	COOH 288.6 eV (±0.2)	Pi-Pi* 290.2 eV (±0.2)	CC C-C sp ² + C-C sp ³	CO C-O+C= O+COO H	CC / CO
LRGO-7.5 mW 5um/s	52.61%	3.71%	33.45%	3.43%	4.41%	2.39%	56.32%	41.29%	1.36
LRGO-7.5 mW 2um/s	57.07%	4.12%	28.92%	2.75%	4.81%	2.33%	61.19%	36.48%	1.68
LRGO-7.5	54.13%	8.78%	25.14%	5.13%	4.58%	2.24%	62.91%	34.85%	1.81

mW
1μm/s

Laser reduction

Figure S1 (a) The image of GO film (yellow color) with LRGO (black area, 1 mm×1 mm). (b) The laser patterned figures on GO film, lines array, the scale bar is 100 μm. (c) The GO sample for thickness measurement under the microscopic (the scale bar is 20 μm).

Figure S2 Survey X-ray photoelectron spectra of GO and LRGOs fabricated with laser power of 3 mW, 5 mW, 7.5 mW, 10 mW and 13 mW at laser scanning speed of 5 μm/s.

Figure S3 (a) The Raman spectra of GO and LRGOs fabricated at laser scanning speed from 0.1 μm/s to 5 μm/s with constant laser power of 5 mW (1 accumulation). (b) The Raman spectra of GO and LRGOs fabricated at constant laser scanning speed of 0.2 μm/s with laser power from 3 mW to 13 mW (1 accumulation). (c) Raman spectrum of LRGO (13mW, 0.2 μm/s, 10 accumulations). (d) Raman spectrum of LRGO (13mW, 0.2 μm/s, 30 accumulations).

Figure S4 XRD analysis of GO and LRGOs at different laser power with scanning speed 5 $\mu\text{m/s}$.

Figure S5 Peak fitted $\text{C}1\text{s}$ XPS spectra of LRGOs fabricated at laser power of 7.5 mW with different scan speed (a) 2 $\mu\text{m/s}$ (b) 1 $\mu\text{m/s}$.

Conductivity test

Figure S6 (a) Illustration of LRG conductivity measurement procedure. (b) The photograph of sample for conductivity test

Figure S7 Graphic illustration of the calculative method for LRG conductivity (L, length of LRGO; W, width of LRGO; T, thickness of LRGO; S, the area of LRGO)

Table S7 Conductivities of LRGO with different scanning speeds at power of 5 mW

Scanning speed	Energy density	Resistance before irradiation	Resistance after laser irradiation	L	W	T	Conductivity
($\mu\text{m/s}$)	($\text{mJ}/\mu\text{m}^2$)	($\text{M}\Omega$)	($\text{M}\Omega$)	(μm)	(μm)	(nm)	(S/m)
2	1.25	480	353	688	1.06	97	19.0
1	2.5	510	108	502	1.31	96	36.9
0.5	5	1000	125	647	1.81	93	30.7
0.2	12.5	505	110	694	2.42	73	35.7
0.1	25	700	61	640	3.25	71	45.5

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Tuning the sub-processes in laser reduction of graphene oxide by adjusting the power and scanning speed of laser

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