Laser Beam-Induced Transient Acoustic Waves in Graphene Oxides

Litty V. Thekkekara* and Ivan Cole

1. Introduction

Laser-induced graphene obtained from graphene oxides (GOs) undergoes a photothermal and photochemical mechanism depending on the irradiation conditions used in the process.[1] It can be observed that the influence of laser beam irradiation in GOs can result in the phase change in the material resulting in morphological changes,[2] refractive index modulation,[3] and electrical conductivity changes.[4] Due to the controllable properties, the laser beam induced graphene from the GOs to find applications in areas, such as optoelectronics,[5] electronics,[4] energy storage,[2,6] microphone diaphragms and artificial throats,[7] holograms,[8] as well as biomedical imaging and therapies.[9]

Earlier, it is reported that during the laser beam irradiation in graphite, a pure form of GOs is influenced by the shock waves, which is a particular case of acoustic waves[10] permanent physical damaging the atomic structure.[11] However, these studies are insufficient to fully understand the laser beam-assisted reduction process in GOs, especially the photochemical process observed with ultrashort pulses and the ultraviolet regime.[12]

Recently, multiphoton ionization in GOs contributing to the photochemical reduction using the femtosecond (fs) laser beam pulses interaction is reported.[13] Recent density functional theory and experimental studies suggest the localized reversible phases in GO material and the wettable GOs with the bond breaking in the material’s atomic structure.[14] Our article explores the generation of laser-induced acoustic waves during GOs’ photoreduction and associated reversible changes in the material. The resultant phase transition without the physical surface damages is demonstrated using an amplified laser system (Coherent Libra and Astrella). The laser beam irradiation conditions used in the studies are a wavelength of 800 nm and a pulse width of 120 fs with different pulse repetition rates.

2. Results and Discussion

In Figure 1a, a schematic of the observed ripple wave generation is given, and the resultant thickness reduction in the GOs is shown as highlighted. During the laser beam exposures with lower fs laser beam pulse repetition rates such as 10 and 5 kHz in GOs, the presence of ripple waves is observed in charge-coupled device (CCD) camera (Figure 1b). These effects are not found during the photoexposures in GOs using the higher repetition laser beam pulses such as 80, 40, and 20 MHz.[13] Figure 1c shows the same region’s image after the laser beam, under the same irradiation conditions, is turned off, which leaves the phase transformed graphene patterns in the thin film. The observed ripple waves are absent, unlike the permanent periodic features observed in graphite.[11] The observation of this phenomenon for different laser beam fluences in GOs under a pulse repetition rate of 5 kHz is given in Figure S2, Supporting Information. The temperature generated during the laser beam interaction in GOs is given in Figure S3, Supporting Information.

Further characterizations on laser-treated GO thin films are given in Figure S4–S8, Supporting Information, to understand the reduction in the material. Figure S4, Supporting Information, details the thermogravimetric analysis of GOs. Different laser beam reduced GO thin films, and porous distribution obtained in laser beam reduced GO thin films using other pulse width conditions. Figure S5, Supporting Information, details the morphological characterizations of the laser beam-treated GOs under different pulse repetition rate irradiations. Physical characterizations of the obtained laser beam-treated GOs under different pulse repetition rates are given in Figure S6, Supporting Information. Transmission profiles of

* Corresponding author.

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Litty V. Thekkekara, Prof. I. Cole
School of Engineering
Royal Melbourne Institute of Technology University
Melbourne 3001, Australia
E-mail: littyvarghese.theekkekara@rmit.edu.au
the obtained films are shown in Figure S7, Supporting Information. Figure S8, Supporting Information, shows the development of an optical bandgap in the laser-treated GO thin films. We have considered different substrates and polarization conditions in the Supporting Information during these studies.

The CCD video images of ripple waves in GO thin films (Supporting Information) under the laser beam fluences are considered to investigate these experimental observations in detail. These observations with the lower pulse repetition rates are used to calculate the acoustic wave distance as a function of time. From this information, we have calculated the acoustic wave speed, \( U_s \), using the formula

\[
U_s = \sqrt{\gamma RT}
\]

where \( \gamma \) is the ratio of specific heat, \( R \) is the Universal gas constant, and \( T \) is the room temperature. The calculated \( U_s \) is around 50 m s\(^{-1}\), which confirms that the observed ripple phenomena are an acoustic standing wave from the standard considerations.[15] It can be observed that there is an enhancement of 66% in the acoustic velocity in GOs[11] in the presence of fs laser beam irradiation.

The acoustic peak pressure, \( P \), generated during this traversal process is related to the laser-induced acoustic wave velocity and can be calculated using Equation (2)[16]

\[
P = \rho_0 U_s \frac{U_s}{C_0} \frac{1}{1.99}
\]

where \( c_0 \) denotes the acoustic velocity of GOs, \( \rho_0 \) denotes the density of the GOs, and the factor 1.99 is calculated empirically. The used numerical values can be found in Table S1, Supporting Information.

The calculations show that as the laser beam fluence and scanning stage speed increase, the acoustic pressure decreases (Figure 2a). A maximum acoustic pressure of 0.11 Pa is observed in GOs with a laser beam fluence of 10 \( \mu \)J cm\(^{-2}\) and a scanning stage speed of 10 \( \mu \)m s\(^{-1}\). Furthermore, the influence of the number of laser beam pulses on the acoustic pressure generation is studied, as shown in Figure 2b. An estimate of 12 pulses in the

Figure 1. Acoustic generation in GO thin film during laser beam interaction. a) Schematic of the fs laser beam-induced ripple wave during the photoreduction of GOs. b) A CCD image of ripple wave generation during the laser beam irradiation in GO thin film. c) Microscopic image of the irradiated laser region in GO thin film without leaving the evidence of ripple waves.

Figure 2. Acoustic pressure generation the laser-induced GO thin film under different conditions. a) PA pressure was calculated during the laser beam interaction in GOs using different fluences and scanning stage movement speeds. b) PA pressure calculated during the laser beam interaction in GOs with a different number of pulses having laser beam fluence of 10 \( \mu \)J cm\(^{-2}\) and a scanning stage speed of 10 \( \mu \)m s\(^{-1}\).
given time is ideal for obtaining maximum acoustic pressure. We have not observed any ripple waves or acoustic pressure below the stage scanning speed of 10 μm s⁻¹. This phenomenon might occur due to a resonance developed from the vibrations of stage movement with specific rates.

Furthermore, theoretical modeling is conducted to understand the fs laser beam irradiation in GOs using the 1D heat transfer model (Supporting Information) to study the observed ripple phenomena in GOs in more detail. In the model, we considered fs laser beam irradiation with consecutive 12 pulses with a repetition rate of 5 kHz in GO thin film of thickness 7 μm. The generation of a ripple wave pattern can be observed with an acoustic pressure of around 0.11 Pa in the XY plane (Figure 3a) and Z-direction (Figure 3b).

However, the temperature profile in GO thin film during a single fs laser beam pulse radiation is around 25 °C (Figure 3c). The heat diffusion in GOs becomes an essential factor in examining the temperature influence on the photoreduction with the increasing number of laser beam pulses (Supporting Information). Figure S3, Supporting Information, shows that the temperature generated during 12 laser beam pulses with 5 kHz interaction in GO thin film is roughly 25 °C. It confirms that the heat diffusion in GOs is lower with fs laser beam pulse and indirectly relates to the lower energy transfer between fs laser beam pulses to GOs, resulting in less removal of oxidative groups.[1a,12a,17] More details on these studies can be found in Supporting information.

These results suggest that the breaking of chemical bonds in the atomic arrangement in GOs termed photochemical reduction during the fs laser beam interactions can be assumed to be contributed from a combination of different processes such as chemical, mechanical, and acoustic with less contribution from temperature depending on the laser beam irradiation conditions used in the process. This observation is different from the reduction in GOs using continuous wave (CW) and nanosecond (ns) lasers, where reduction is mainly contributed by the thermal process.[18] A comparison between the experimental and theoretical calculations of GO thin film’s acoustic pressures of varying thickness can be found in Figure 3d and Figure S4, Supporting Information, which co-relates with the earlier experimental and numerical results.

Further photoacoustic (PA) studies are conducted to obtain a detailed survey of the GO thin film’s observed acoustic waves phenomena. The details of the measurement can be found in the Experimental Section, and the schematic of the measurement setup can be found in Figure S4, Supporting Information. It is a direct approach to understand the acoustic wave generation and properties in materials.[19]

Figure 4a shows the PA signal generation in a GO thin film thickness of 7 μm, representing a periodic sinusoidal form in the laser beam irradiation duration. This feature disappears as the laser shutter is closed. However, frequency-dependent measurements are conducted in these thin films to understand the...
magnitude in decibels of generated acoustic waves. In this aspect, thin film thickness has a more substantial influence. In a GO thin film thickness of 7 μm, over a 70% magnitude is observed for a broadband acoustic frequency range, as shown in Figure 4b, which includes the human frequency range (20 Hz–20 kHz). This observation is expected to be due to stronger resonance, which generates stronger PA signals in the thicker films compared with the lesser thickness film. These results can be beneficial to future broadband PA sensing applications. It is reported that the sonic waves can influence the phase transformation in graphite-related compounds.\(^\text{[20]}\)

### 3. Conclusion

In conclusion, this study shows an acoustic standing wave contribution to the photochemical breakdown and a reversible nature in GOs, leading to a metastable phase with the lower repetition rate fs laser beam pulses. Furthermore, we can understand that these lead to insufficient energy to annihilate the oxygen groups from the GO atomic structure in absolute in GOs, leading to a lesser crystallization in the laser-induced graphene thin film with a transition from photothermal toward photochemical phenomena as the pulse repetition rate of fs laser beam irradiation decreases. With the efficient tuning of acoustic waves using the laser beam irradiation conditions, the phase transition in the laser-induced graphene thin film can be controlled. These transient phenomena can find applications in broad areas such as optical data storage\(^\text{[21]}\) and optical neural chips.\(^\text{[22]}\) A rewritable graphene optical data storage can be developed using a localized reversible phase of the laser-treated GO thin film. Similarly, using controlled acoustic pressure, optical communication between artificial neural dendrites can be studied.

### 4. Experimental Section

**Materials:** Concentrated GOs (4 mg mL\(^{-1}\)) were purchased from Sigma-Aldrich and diluted in water to obtain a molar concentration of 1.3 mg mL\(^{-1}\). The 2 mL of diluted GO thin film of the concentration of 1.3 mg mL\(^{-1}\) was drop-casted on a glass and polydimethylsiloxane substrates and GO thin film along which was prepared by the vacuum filtration method and later removed from the filter. The obtained thin film was dried at 60 °C using a heat plate in the atmospheric conditions. The thickness of the GO thin films was around 3, 7, and 10 μm. The results provided in this study were based on the GO thin film coated on a glass substrate, on which the effect was more pronounced.

**Methods:** Laser beam interactions with GOs were studied using a custom-built laser setup using mode-locked fs lasers (Chameleon, amplified Astrella, and Libra) wavelength of 800 nm and a pulse width of 120 fs with the pulse repetition rates varying from 80 MHz to 5 kHz using a pulse picker. The used pulse picker is an electro-optic modulator that helps pick the required number of pulses from the mode-locked laser’s pulse train. The GO thin film was deposited on a glass slide and fixed on a scanning stage, which has a travel accuracy of up to 1 mm. Depending on the computer-controlled stage movement conditions, we had been given the stage can make X–Y movements. An oil objective of numerical aperture 1.4 was fixed in a Z-axis movable optical holder, and 100X magnification was used, and a CCD camera (Thorlabs) was used to record the propagating laser shock-induced PA waves generation in GOs in real time. We have observed that the laser beam polarizations do not affect the generation of the acoustic waves in GO thin films.

To understand in detail the on-going process, we have done PA measurement by modifying the existing setup. The experimental setup for PA measurements is shown in Figure S1, Supporting Information. An fs laser beam (Astrella) wavelength of 800 nm, a pulse width of 120 fs, 5 kHz pulse repetition rates, and 0.35 NA objective were used for the measurements. The thickness of GO thin film and laser beam fluences were varied to understand the generation and amplitude of transient PA signals. A PA resonant cell was constructed for the measurements based on the resonant frequency range in the GOs of different thicknesses. The sample was kept inside the PA cell. A condenser microphone of 6 mm (RS Pro Omni-Directional Microphone Condenser) for measuring the broadband frequency from 20 Hz to 20 kHz with a sensitivity of 42 dB was placed at 3 mm from the sample inside the PA cell. The PA cell is fixed on the scanning stage. The PA signals were detected and amplified using a preamplifier (Stanford Research Systems). The acquired signals were recorded at a sampling rate of 10 GS s\(^{-1}\) and analyzed using an oscilloscope (Tektronix). A CCD camera (Thorlabs) was used to record the laser shock-induced PA waves. The theoretical model used to calculate the temperature profile generated in the GO thin film during fs laser beam pulse and acoustic pressure generation during the process is discussed in detail in Section 1, Supporting Information. The scanning electron microscopy (SEM) measurements were performed using Philips XL30 at 15 kV, and the transmission electron microscopy (TEM) measurements using the JEOL 1010 instrument in which samples were drop-cast onto-formvar grids. Thorlabs CCD camera was used to observe the laser writing in the GO thin film.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
L.V.T. proposed the idea, designed, and performed simulations and experiments. Both authors were involved in the data analysis and writing of the manuscript.

Keywords
femtosecond laser beam-matter interactions, graphene oxides, photoacoustic, transitory phenomena

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