Eye-friendly reduced graphene oxide circuits with nonlinear optical transparency on flexible poly(ethylene terephthalate) substrates
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Winco K. C. Yung, Guijun Li,* Hai Ming Liem, Hang Shan Choy and Zhixiang Cai

The selective reduction of graphene oxide (GO) with direct laser writing is a rapid and efficient process to pattern conductive tracks for flexible electronic circuit applications. Here we report novel eye-friendly reduced graphene oxide (rGO) conductive tracks on transparent and flexible poly(ethylene terephthalate) (PET) substrates synthesized by one-step laser reduction of graphene oxide in an ambient environment. Resistivity as low as $1.07 \times 10^{-3} \, \text{m}$ has been achieved for a 20 nm thick rGO film after the industrial-grade 1064 nm Nd:YAG laser treatment. Fingerprints of the synthesized rGO were verified by Raman spectroscopy with an increased intensity ratio of the 2D band over the G band, and the deoxygenation results were examined using both X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) characterization. The rGO synthesized by this infrared laser reduction showed increased absorption toward a shorter wavelength of up to 96% in UV regions, which can significantly protect human eyes from high energy light hazards. Electronic circuit tracks with rGO synthesized with this 1064 nm laser patterning process can provide novel methods for the fabrication of future eye-friendly flexible electronics with nonlinear optical transparency.

Introduction

Graphene is one of the most essential materials for next generation transparent and flexible electronics. As a zero band gap material, the monolayer graphene has excellent conductivity. With zero effective mass, it also possesses the highest mobility ever recorded. Thus graphene has been intensively studied for various applications in emerging electronics, such as transistors, photodetectors and solar cells. Graphene can be synthesized by chemical vapour deposition (CVD), mechanical exfoliation from graphite, and reduction of graphene oxide. Using the CVD and mechanical exfoliation method we can synthesize high-quality single crystal graphene with almost no defects; however, the production rate is relatively small to satisfy the requirement of mass production. Although the rGO synthesized using the modified Hummers method may include some defects, the low cost and high throughput features still make rGO feasible for mass production applications.

Intensive studies have been focused on synthesizing rGO using photo deoxygenation methods during the past five years as summarized in Table 1. The KrF excimer laser with a wavelength of 248 nm and a pulse width of 20–25 ns was intensively investigated to reduce GO under $\text{H}_2$, $\text{N}_2$, water solutions, and even in an ambient environment. The ultrahigh energy of photons from the excimer laser can directly break the oxygen bonds attached to graphene, and can facilitate the reduction of GO to rGO. Meanwhile, the femtosecond laser possessing ultra-high photon energy within a short duration in the time-domain was also intensively studied to reduce GO. With the pulse width ranging from 100 to 120 fs, rGO was successfully synthesized using the femtosecond laser in both water solutions and an ambient environment. Simultaneously, the Nd:YAG laser at 1064 nm together with its second harmonic generation (SHG) and third harmonic generation (THG) lasers at 532 and 355 nm were also studied to reduce GO. With a short wavelength of 355 nm, the blue THG laser could effectively reduce GO in an ambient and an $\text{N}_2$ environment using a mechanism similar to the excimer laser. With a lower energy at 532 nm, the green SHG laser was still capable of reducing GO in an ambient/$\text{N}_2$ environment and water solutions. Using phase lock loops, the 1064 nm Nd:YAG with 10 picosecond pulse width can still synthesize rGO in an $\text{N}_2$ environment. However, the fundamental 1064 nm with a pulse width of 7 ns did not show a significant reduction of GO in aqueous solution. The possible mechanism is due to the high absorption of 1064 nm in water, so the photon energy may not be efficiently transferred into GO.
There have been increasing demands of flexible electronics for wearable devices, and the fabrication of low cost high quality conductive circuits is one bottleneck to supply these products. However, there are few reports on the fabrication of flexible electronics based on low cost GO with the laser reduction using industrial-grade lasers in an ambient environment. The intensive studies for the reduction of GO using the excimer or femtosecond laser on GO may be rather expensive for practical applications in industry. Therefore it is crucial to develop industrial-grade laser reduction techniques for patterning graphene tracks on flexible substrates. PET is one of the most widely used plastic materials at the operating temperature below 250 °C. Meanwhile, PET possesses ultralow transmittance at the near IR range and the adsorption at 1064 nm is 103 times lower than the widely used transparent indium tin oxide (ITO). Meanwhile, graphene oxide has been proved to possess high absorption at the IR range. Consequently, for a PET substrate coated with GO, infrared lasers can selectively interact with GO without affecting the properties of the underlying PET substrate.

Here the industrial-grade 1064 nm Nd:YAG laser reduction of GO on the PET substrate in an ambient environment was systemically investigated. The GO was first spin-coated on the transparent PET substrate, and then selectively reduced using an Nd:YAG laser in an ambient environment. The electrical resistivity was measured to be 1.07 × 10^{-4} Ωm determined by standard four-wire measurement. Porous rGO structures after the laser treatment were revealed by the scanning electron microscopy (SEM) characterization. Fingerprints of rGO were shown by the increased intensity ratio of the 2D band over the G band by Raman spectroscopy analysis. A dominant decrease of C=O bonds was proved by XPS and FTIR analysis. Optical transmittance results showed that these conductive rGO tracks synthesized by infrared laser treatment exhibited a larger absorption rate up to 96% towards higher energy lights. These nonlinear transparent and flexible electronic circuits fabricated by the proposed industrial-grade laser process can work as human eye-friendly filters against the hazards from high energy lights.

### Experimental

#### rGO synthesis

GO aqueous solution was used as purchased from Graphene Laboratories Inc. NY, with over 60% as a monolayer, a concentration of 500 mg L^{-1} and a flake size ranging from 0.5 to 5.0 μm. The GO solution was spin-coated at 700 rpm on a 3M PET substrate for 60 s. Then the sample was heated at 95 °C for 30 min before laser treatment. A Lasertec Nd:YAG laser at 1064 nm with a repetitive rate of 5 kHz was used to reduce GO and the laser energy density was measured to be 150 mJ cm^{-2}. Circuit tracks were patterned on GO films by the computer-aided movement of the laser spot as illustrated in Fig. 1(a) and (b).

#### Materials characterization

The thickness of the GO film before and after the laser treatment was measured using a Wyko NT9000 optical profiling system with sub-nanometer resolution. The microstructures of GO and rGO samples were studied using a JEOL-5600LV SEM. The vibration modes of the GO and rGO were measured using a Renishaw 2000 × 50 confocal Raman spectrometer with 514 nm laser excitation. The resistivity of the rGO circuits was studied by standard four-wire measurement using an Agilent 4338B multimeter. The chemical composition of GO before and after the laser treatment was characterized using an AXS Ultra XPS from Kratos Analytical in the range of 1–1350 eV. Fourier transform infrared (FTIR) spectra were obtained using a Perkin-Elmer FTIR Multiscope Spectrum 100T spectrophotometer with KBr disks in the range of 500–4000 cm^{-1}. The UV-Vis transmittance of the rGO sample was characterized using a Perkin-Elmer LAMBDA 650 UV/Vis spectrophotometer ranging from 350 to 800 nm.

### Results and discussion

#### Electrical resistivity

The as-prepared GO film on a PET substrate shows brown color as shown in Fig. 1(c) and the corresponding thickness of GO was measured to be 90 nm revealed by the optical profiler. After the laser writing, the patterned area shows grey color as shown in Fig. 1(b).

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>Pulse width</th>
<th>Duration</th>
<th>Environment</th>
<th>Reduction</th>
<th>Ref.</th>
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<tr>
<td>248</td>
<td>20 ns</td>
<td>20–100 pulses</td>
<td>50 mTorr H₂</td>
<td>Yes</td>
<td>7</td>
</tr>
<tr>
<td>248</td>
<td>25 ns</td>
<td>10–15 pulses</td>
<td>500 sccm N₂</td>
<td>Yes</td>
<td>8</td>
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<tr>
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<td>5 min</td>
<td>Water</td>
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<td>9</td>
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<tr>
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<td>20 ns</td>
<td>200 μm s⁻¹</td>
<td>Ambient</td>
<td>Yes</td>
<td>10</td>
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<td>355</td>
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<td>20 s</td>
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<td>16</td>
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<tr>
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<td>10 s</td>
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<td>Yes</td>
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<tr>
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<td>Ambient</td>
<td>Yes</td>
<td>15</td>
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<tr>
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<tr>
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<td>20 s</td>
<td>Ambient/N₂</td>
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<td>600 µs</td>
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<td>1–400 pulses</td>
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<td>1–60 min</td>
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<tr>
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<td>120 fs</td>
<td>900 µs</td>
<td>Ambient</td>
<td>Yes</td>
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<tr>
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<td>N₂</td>
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<td>7 ns</td>
<td>0–2 min</td>
<td>Water</td>
<td>No</td>
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</table>

### Table 1 Summary for the laser reduction studies of GO
in Fig. 1(d) and the thickness was reduced to 20 nm measured by the optical profiler. The resistivity of the laser patterned rGO was measured by standard four-wire measurement using conducting copper tapes as electrodes. The typical resistivity was measured to be $1.07 \times 10^{-4}$ $\Omega$m and $500 \, \Omega$ sq$^{-1}$ after 1064 nm laser reduction with an energy of 150 mJ cm$^{-2}$.

**SEM characterization**

The circuit tracks patterned by Nd:YAG laser were examined using SEM, as shown in Fig. 1(b). The grey color regions represent GO and the black color regions represent rGO. The higher resolution SEM images of GO before and after laser treatment are shown in Fig. 2 respectively. Smooth surfaces with higher folding boundaries due to the restacking of layers of GO are observed in GO, as shown in Fig. 2(a). This kind of morphology is uniform across large areas as illustrated in the zoom-out image in the inset of Fig. 2(a). After laser treatment, the surfaces of rGO become highly porous, as shown in Fig. 2(b). Grains are widely emerged across larger areas with crumpled and rippled structures, as shown in the zoom-out image in the inset of Fig. 2(b). The possible explanation of the morphology change might be due to the deoxygenation process during the laser treatment. rGO released oxygen and this reaction induced defects among the rGO. As a result, a porous surface was left after the laser reduction process.

**Raman characterization**

The fingerprints of GO before and after the 1064 nm laser treatment at energy density of 150 mJ cm$^{-2}$ are identified by
Raman spectroscopy with representative spectra as red and blue curves respectively in Fig. 3. The characteristic peaks at 1358, 1595, and 2691 cm$^{-1}$, corresponding to D, G, and 2D bands respectively, are used to recognize the GO and rGO. The G band at 1595 cm$^{-1}$ represents the sp$^3$ hybridization of the carbon atoms in GO. The D and 2D bands both fit with symmetry Lorentzian curves. After laser reduction, the intensities of D and G bands are doubled. Meanwhile, the 2D intensity is increased up to 2.3 times after laser reduction. So the intensity ratio of the 2D band over the G band is increased, indicating more graphene is synthesized after the laser reduction.24 Meanwhile, the full width at half maximum (FWHM) of the 2D peaks after Lorentzian fitting is 64 cm$^{-1}$. Previous work suggested that the 2D peaks fitted with a single Lorentzian profile having a typical FWHM between 50 and 65 cm$^{-1}$ could reveal the presence of turbostratic graphite,16 which is composed of multiple randomly oriented graphene sheets.25 To account for the crystalline quality of the GO films in terms of order parameters before and after laser-reduction, the mean domain sizes ($L_a$) in graphene, relating to the D/G intensity ratio, are used.26,27 The empirical relation $L_a$ (nm) = $2.4 \times 10^{-10} \times \lambda_1^4 (I_D/I_G)^{-1}$ is re-examined, where $\lambda_1$ is the probe laser wavelength (nm), $I_D$ and $I_G$ are the Raman area intensities of the D and G bands. From the red and blue spectrums in Fig. 3, $L_a$ values of 18.8 nm and 28.2 nm were calculated for the un-reduced and the laser reduced GO. An increase in the $L_a$ value suggests that the laser-reduced graphene oxide evolves to a more ordered state with fewer defects.27 It can be inferred that the removal of oxygen atoms from GO films takes place without causing any damage to the lattice, which is consistent with the reported theoretical calculation results.28

**XPS characterization**

The chemical compositions of GO films before and after laser reduction are revealed by XPS spectra with curve fittings as shown in Fig. 4(a) and (b) respectively. The overall atomic ratios of oxygen to carbon are dramatically decreased from 3.8 to 0.09 after laser treatment, indicating dominant deoxygengation process occurred. The characteristic peaks at 284.5, 285.6, 287.2, and 289.0 eV correspond to C–C, C–O, C=O, and O–C=O functional groups respectively.29–31 The intensity of the C–C bond at 284.5 eV shows similar orders of amplitude before and after the laser reduction, indicating that the carbon atoms in GO are not etched away during the laser reduction process. In comparison, the C–O bond at 285.6 eV and the O–C=O bond at 289.0 eV show a slight decrease after the laser treatment, indicating the less deoxygenation of these two bonds during the laser reduction process. The most significant decrease is found to be the C=O bond at 287.2 eV where the intensity is greatly reduced. Thus it can be inferred that the 1064 nm laser treatment is mainly deoxygenating the C=O bonds in GO.32

**FTIR characterization**

In order to further investigate the deoxygenation process after the laser reduction, the chemical components of the GO before and after the laser treatment were also studied using FTIR and shown in Fig. 5 as red and black curves respectively. Different types of oxygen containing functional groups on GO are observed at 3600 cm$^{-1}$ (O–H stretching vibration), at 1720 cm$^{-1}$ (C=O stretching vibration), at 1610 cm$^{-1}$ (un-oxidized graphitic domain skeletal vibration), at 1230 cm$^{-1}$ (C–OH stretching vibration) and at 1058 cm$^{-1}$ (C–O stretching vibration).33 The C=O stretching vibration peak at 1720 cm$^{-1}$ is significantly smoothed after the
laser treatment, indicating strong removal of C–O bonds by laser reduction. Meanwhile, the peaks of C–O and C–OH remained with similar amplitudes after the laser reduction. The characterization for the deoxygenation process by FTIR is consistent with the above XPS results. Significant amounts of C–O bonds are removed while fewer C–O and C–OH bonds are influenced, which may be due to the selective reduction of the current 1064 nm laser. During the laser treatment process, the absorption rates of GO exposed to different photon energies would be different. High energy lasers such as femtosecond or excimer lasers were reported to be more powerful to reduce the C–O bonds rather than C–Q bonds. Measurements performed with samples undergoing laser treatment showed significant nonlinear absorption for high energy lights. It is thus trustworthy that this kind of conductive rGO with such nonlinear transmittance at UV and visible ranges would become promising materials for emerging flexible and transparent electronics, especially for emerging wearable visual display devices.

**Conclusions**

Nonlinear optical transparent and electrical conductive rGO electronic circuits on flexible PET substrates were fabricated by a one-step laser reduction and patterning process in an ambient environment using an industrial grade 1064 nm Nd:YAG laser. The microstructures of the rGO after laser treatment showed significant porous structures as evinced by SEM. Dominant graphene synthesis was revealed by the increased 2D over G ratios in Raman spectroscopy. The deoxygenation process with significant removal of C–O bonds was verified by XPS and FTIR analysis. The resistivity of the laser reduced GO was measured to be as low as $1.07 \times 10^{-4}$ Ωm. The UV-Vis spectrum of the laser treated rGO showed a nonlinear optical transparency with enhanced absorption as the photon energy increased. These selective transparency materials can efficiently reduce the hazards from high energy lights and protect human eyes from short-wavelength light radiation, which is crucial for future transparent and flexible electronics, especially for visual applications such as wearable displays and electronic glasses. Besides, this maskless laser direct patterning method is capable of structuring any arbitrary shapes drawn by computer-aided designs for the fabrication of patterns such as conductive tracks, resistors, and capacitors. Future work will include patterning rGO based electronic devices on other transparent substrates, such as polydimethylsiloxane (PDMS), for potential on-chip biomedical applications.
Acknowledgements

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Notes and references