Comparison of low cost lasers for graphene oxide thin films reduction

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Abstract. In this work we made reduction of graphene oxide films with different low-cost lasers (near IR (1060 nm) and blue (445 nm) to investigate possibility of such films usage for flexible electronic and nanoelectronic applications. We successfully showed possibility of graphene oxide reduction with both types of laser but blue laser showed better uniformity of reduced graphene oxide film parameters including film morphology, resistance and Raman intensity ratios. We showed that reduction with near IR laser spills out into large nonuniformity of resistance with relatively high values. Thus the usability of commercially available laser facility for graphene oxide modification without adjusting control settings (on hardware and software levels) is poor. On the other hand, relatively laboratory device based on low-power blue laser showed much better usability an it’s perspective to future market of low-cost modification facilities for thin carbon-based films.

Keywords: graphene oxide, reduced graphene oxide, laser reduction, aerosol deposition, nanoelectronic, flexible electronic.

1. Introduction

New modern research and engineering fields like flexible [1] and organic electronics [2], energy storage [3], sensors [4], functional [5] and classic composites [6] etc. requires new approaches in material processing and modification. One of the other important trends in material processing today is digital manufacturing technologies like 3D printing [7], CNC machines [8] etc. But most of such devices for processing operates with bulk or macrosized materials. And there is a need in processing methodic [9] and devices adapted for functional materials processing. There are some new approaches [10] and methodics [11] that allows to modify composite materials to give them additional functionality [12]. But main lack of these approaches is its nonlocality which is not enough for electronic and sensing applications.
Among possible methods of functional materials processing one of the most perspective is laser modification. Depending on laser parameters it is possible to treat such perspective components of functional materials as nanoparticles [13], carbon nanotubes [14], graphene [15] and its derivatives [16] etc.

For the future functional materials (in particular for usage in wearable electronics) one of the most promising class of components that meet these conditions is graphene and its derivatives like graphene oxide due to its flexibility, conductivity and presence of functional groups [17] in case of graphene oxide or reduced graphene oxide.

In this article we experimentally showed possibility of successful graphene oxide processing. Graphene oxide up to day is better decision for conductive film formation due to much easier transfer process with variety of possible substrates. Pure graphene transfer is not an easy process [18] and it doesn’t work well with flexible polymer substrates or such basis of composite materials as glass and carbon fibers. Another great advantage of graphene oxide (and reduced graphene oxide) is abovementioned presence of different functional groups that give possibility to couple with nanoparticles [19], biological molecules [20] or different polymers [21].

There are two key operation in graphene oxide based conductive film formation: graphene oxide deposition (that should be as uniform as possible) and reduction (that should be precisely controllable). Graphene oxide can be deposited on the substrate by many techniques including drop casting [22], rod coating [23], Langmuir-Blodgett technique [24], spin-coating [25] etc. But among them all one most promising is aerosol deposition due to possibility of formation of very thin but uniform and large area film [26] on variety of substrates including glass and carbon fibers. Moreover, this method has an advantage on drop-casting and spin-coating in less solution consumption. Nevertheless, to obtain best theoretical uniformity we tried to use spin - coating method [27].

Development of wearable electronic devices requires formation of the conductive layer and it’s preferable to use such method that give possibility to precisely control modification parameters. In case of graphene oxide based wearable electronic devices there is a need to form conductive pathways by reduction of graphene oxide with predetermined pattern.

Graphene oxide reduction could be done by different methods, but two most known methods are chemical [28] and thermal [29] reduction. Conventional reduction methods include graphene oxide processing in reducing agents as hydrazine, ascorbic acid etc., or thermal annealing in inert atmosphere. Nevertheless, these methods don’t allow to perform local reduction and, thus, they are not suitable for functional device mass fabrication.

Promising reduction method being developed last decade is graphene oxide laser treatment [30], realizing photochemical [31] or thermal reduction [32] depending on laser wavelength, energy density and pulse width. Femtosecond laser pulses allows to attach or remove various functional groups [33] via photochemical reaction, but such method has significant drawback: high price of laser system. On the other hand, laser induced thermal reduction, that can be performed by much cheaper micro/nanosecond pulse lasers or even continuous wave laser, allows to reduce graphene oxide directly on flexible substrate due to rapid local heating. Concept of laser reduction combines fast processing, controllable reduction degree, possibility of patterning and applicability for a wide range of substrates.

In this article we show possibility of local modification of graphene oxide films by using microsecond pulsed laser with different wavelength (blue and near IR). As we assume it’s possible to use both type of this lasers for local modification of thin graphene oxide films with better results obtained by blue laser.

2. Materials and methods

Water GO suspension (4.1 mg/ml) produced by improved Hummers method was purchased at LLC “MIP Graphene” (Yakutsk, Russian Federation) [34]. Suspension was further diluted in deionized water to 0.5 mg/ml concentration for spin coating deposition.

We used poly(ethylene terephthalate) (PET) substrates as a promising material for further development of flexible and cheap bio- and gas sensors with reduced graphene oxide active layer. For spin coated
films we used high opacity PET film without surface treatment. Substrates with 20 x 20 mm dimensions were precleared with 2-propanol and water. Deposition of the suspension was performed by Spin-NXG spin-coater (Apex Instruments) with maximum 2000 rpm.

Laser treatment was carried out by two facilities:
1) Commercially available Mercury III laser engraver (GCC Laser Pro, Taiwan) with 1060 nm CO2 laser with 25 W maximum power controlled by pulse width modulation (PWM) at 5 MHz frequency (Synard 48 Series, USA) and pulse length 1 µs (also can work as continuous wave mode). Output power was ranged from 2% to 6% of maximum power (25 W), stage movement velocity was varied from 25% to 100% of maximum possible.
2) own-designed system with 445 nm solid-state laser facility with motorized table [35]. Output laser power was varied in 10-400 mW range by pulse width modulation (PWM) at 30 MHz frequency. Pulses width ranged from 1 to 20 µs. Treatment time in a spot (~1.5·10³ µm²) was constant 30 µs.

Raman spectroscopy was used for reduction process survey by estimating relative intensities of specific GO and rGO Raman peaks $I_D$ (1350 cm⁻¹), $I_G$ (1582 cm⁻¹), and $I_{2D}$ (~2700 cm⁻¹). To obtain Raman spectra and optical images we used Centaur U HR spectrometer (Nano Scan Technologies Ltd, Russia) with Mitutoyo lens with x50 magnification and aperture NA 0.55. We also used FTIR Nicolet iS10 spectrometer (ThermoFisher scientific, USA) to investigate presence of different functional groups in reduced films.

Resistance of reduced films was measured by two-contact method with IPS 16 (CJSC EKSI5, Russian Federation).

3. Results and discussion
3.1 Laser reduction by near IR laser

As it mentioned before, we used Mercury III laser engraver to reduce graphene oxide film with different parameters. The Mercury III laser engraver give possibility to vary movement speed of engraving head (i.e. laser) and power of the laser in percent to the maximum power (about 40 W laser) with increments of 1%. As we find out power about 7% of maximum power and higher leads to full destruction of the graphene oxide film and PET substrate. Reduction in this case could be done only in a range from 2 to 6 % with the same increment. So we formed a set of structures with 25, 40, 60, 80 and 100 % movement speed for each of 2, 3, 5, 6 % of laser power.

As a result, we observed differences in surface morphology, resistance and Raman spectra of these structures. By this results we identified 5 groups or reduced films with specific parameters. First group consists of almost nonreduced films with surface morphology similar to pure graphene oxide (figure 1a). These structures have resistance about 6 MOhm or more and can be obtained in case of low laser power (2-3%) and low movement speed (25-40%) (see blue cells in table 1). So we can mention that under low laser power and movement speed reduction threshold can’t be exceeded.

Second morphology type have locally reduced graphene oxide conductive pathways with up to 0.5 mm length (200-300 µm average) with clearly seen graphene oxide film between reduced areas (figure 1b). As we can mention in this case reduction threshold is exceeded but in some local areas due to local nonuniformities of a graphene oxide films. So in this case reduction take place only in top layers of graphene oxide film and it doesn’t form continuous pathways on the macrosize. Due to the fact that long conductive channels are not formed, such structures have a high resistance from 1.5 to ~5 MOhm (yellow cells in table 1). Nevertheless, reduced areas in this morphology have Raman spectra close to the fourth type of morphology with relatively high intensity of 2D peak and low D peak (figure 2c).
Third morphology type is reduced graphene oxide with conductive channels with caverns inside laser pathway (figure 1 c). According to Raman spectroscopy (figure 2 b) this is the most preferable type of reduction that can be done on laser engraver. This morphology type has resistance in range from ~70 kOhm to ~900 kOhm. Raman spectra in this case indicate the presence of more defects in the structure, and according to [36] have the largest amount of functional groups. These structures marked green in table 1. We can also note that in this case only small wrinkled graphene oxide areas are observed between reduced pathways. We attribute this fact to the higher heating of the film on larger areas that lead to formation of longer pathways independent of local GO film nonuniformity. But heating in this case is
not enough to obtain form highly structured multilayer graphene grains like in fourth type of morphology. This type of reduced film has best perspective for nanocomposite formation due to the maximal number of functional groups. Among possible applications of such type of reduced graphene oxide film chemical or biological sensors are preferable. Fourth morphology type have clearly seen conductive pathways without caverns (figure 1 d) and with relatively high graphitization level according to Raman spectra (figure 2 c). Such structures have resistance from ~27 kOhm to ~700 kOhm (orange cells in table 1). From table 1 it is clearly seen that this type of morphology usually obtained with 5-6 % of laser power with all movement speed except 60 and 100 % (in the last case the destroyed morphology is like an extremal type of the same morphology). In this case we can observe low Raman intensity of D peak and relatively high intensity of 2D peak. We can attribute this to the formation of highly structured grains of a few-layer graphene.

Fifth type of morphology looks similar to fourth but with local destruction of the whole film. Such structures are obtained only in case of high movement speed. This fact can be explained by the excess of ablation threshold due to high laser fluence in one point.

Figure 2. Raman spectra and morphology of near IR laser reduced GO films.

Figure 3 with of I_D/I_G and I_2D/I_G ratios dependence of the laser power and laser movement speed have very good coincidence with table 1. We can mention that nonreduced structures have I_D/I_G ratio about 1,0 and I_2D/I_G ratio ~0,35. Locally reduced films have variations in peaks intensity ratios from 0,75 to more than 1,1 in case of I_D/I_G and from 0,45 to 0,68 in case of I_2D/I_G. Structures that have best conductivity to functional groups presence relation shows have more than 1 I_D/I_G ratio and 0,48-0,55 I_2D/I_G ratio. Highly structured and most conductive structures have about 0,5-0,6 I_D/I_G ratio and 0,7-0,8 I_2D/I_G ratio. In case of film destruction, we once again observe variations in relative peak intensity with from 0,8 to more than 1 I_D/I_G ratio and from 0,35 to 0,6 I_2D/I_G ratio.
As a result we find near IR laser parameters for formation of relatively high conductive reduced graphene oxide films that can be used in different electronic applications (flexible electronics for example). Another relatively narrow group of parameters is perspective for functional nanocomposite formation that can further be used in different applications, for example chemical or biosensors.

Table 1. Resistance of spin-coated reduced graphene oxide structures vs laser power and movement speed (blue cells – nonreduced GO; yellow cells – partly locally reduced GO; green cells – slightly reduced GO with low I_{2D}, orange cells – highly reduced GO (high I_{2D}, low I_{D}), red – GO reduced with film destruction).

| Laser Power, % to max | Movement speed, % to max | 25 | 40 | 60 | 80 | 100 |
|------------------------|--------------------------|----|----|----|----|-----|
| 6                      | 77 kOhm                  | 40,3 kOhm | 548 kOhm | 674 kOhm | 3.34 MOhm |
| 5                      | 27,5 kOhm                | 41,5 kOhm | 198 kOhm | 108,1 kOhm | 755 kOhm |
| 3                      | 10 MOhm                  | 8,2 MOhm | 4,78 MOhm | 891 kOhm | 1.4 MOhm |
| 2                      | 13 MOhm                  | 6 MOhm | 1,50 MOhm | 69,8 kOhm | 10,4 MOhm |

3.2 Laser reduction by microsecond pulsed laser

We made series structures modified with blue (445 nm) 600 mW laser power and pulse length 2.5 µs (laser fluence 1.5 µJ) and other modified with same laser power, but pulse length was 150 µs (fluence 93.4 µJ) laser spot size was 40 × 15 um in all cases.

Surface morphology of areas with low and high reduction level is on figure 4 (a) and (b) respectively. In case of low reduction level one can clearly see that structure consist of slightly overlapping laser traces on the whole area of the frame. In case of high reduction level overlapped laser traces forms line-shaped conductive pathways with some distance between them.

Comparing graphene oxide films resistance reduced with near IR laser and blue laser we can notice significant difference in resistance. In case of graphene oxide, reduced with near IR laser resistance of successfully reduced areas varied from 27 kOhm to ~900 kOhm, whereas in case of pulsed lased we obtained resistance about 6 kOhm average (with range from 4 to 12 kOhm). We assume this effect to
the laser wavelength possibility of more precise laser parameters control. Another important fact is that possible step in control software of laser engraver is too big to work with relatively thin films.

![Image of surface morphology](image1.jpg)

**Figure 4.** Optical image of surface morphology of reduced graphene film in sensitive (a) and contact (b) area of sensor device.

So in general it’s possible to reduce graphene oxide with “ready-to-use” laser systems but it’s preferable to have more precise control of laser parameters. Another possible factor that provided a large variation in graphene oxide structures reduced with near IR laser is local nonuniformity of the initial film. We also observed poor adhesion of graphene oxide films reduced with near IR laser to the substrate, whereas in case of blue laser reduction adhesion is good enough.

![Graph of ID/IG ratio](image2.jpg)

**Figure 5.** $I_D/I_G$ ratio for low fluence area (a) and high fluence reduced GO film (b).
From figures 5 and 6 we can notice, that in case of reduction with low fluence ID/IG ratio lies in the range from 0,80 to 1,04 with statistics maximum at 0,98 to 1,00 whereas for high fluence it is in range from 0,5 to 1,1 with maximum at 0,5-0,7. Intensity of I2D/IG lies in range from 0,50 to 1,00 for low fluence, whereas for high fluence it’s form 0,45 to 0,8. Statistic maximums in case of I2D/IG are 0,70 to 0,80 for low fluence and 0,65 to 0,70 for high fluence. According to the previous results with near IR laser we can see that ID/IG and I2D/IG ratios of areas with high conductivity and with high amount of functional groups are similar for both laser types. Near IR laser gives ID/IG ratio about 1 or more for areas with high amount of functional groups and blue laser gives 0,98 average, I2D/IG ratios for same cases are 0,48-0,55 (near-IR laser) and 0,6 (blue laser). For higher reduction these parameters are about 0,5-0,6 ID/IG ratio and 0,7-0,8 I2D/IG ratio (near IR laser) and average 0,6 ID/IG and 0,7 I2D/IG (blue laser).

We obtained FTIR spectroscopy data from both areas obtained by blue laser irradiation (Figure 6). From Figure 6 we can mention significant difference from spectra with low and high reduction level. Main difference is in clearly seen peak at ~1720 cm⁻¹ in case of low reduct level. This peak should be attributed to C=O carboxyl and carbonyl groups according to [37]. I.e. in case of low laser fluence we observe conductive area with some residual carboxyl functional groups that is the main goal for such application of reduced graphene oxide films as different sensors (especially biosensors) due to possibility of covalent coupling of sensitive agents through these groups. We can also observe slight broad peak at ~ 3400 cm⁻¹ that could be attributed to O-H stretching vibrations, i.e. hydroxyl groups presence [38]. Minor peaks at 2847 cm⁻¹ (symmetric) and 2917 cm⁻¹ (asymmetric) are −CH2 absorption band that was split into two sub-bands and can be assigned to alkyl moieties (as a result of the reduction of COOH to -CH3 segment) [39]. Wide band at about ~ 1080 cm⁻¹ appears due to the presence of hydroxyls [40].

It is important to sign that we don’t see any significant peaks of the area reduced with high fluence, that mean that this area have much higher graphitization level and its IR spectra up to 3000 cm⁻¹ is very similar to those obtained by Mingru Su et al. from Si/Graphite® Graphene composite [41].

![Figure 6. I2D/IG ratio for low fluence area (a) and high fluence reduced GO film (b).](image_url)
to results of Raman spectroscopy this area have much lower level of defects with quite noticeable 2D peak which means that graphitization level of this area is higher than in case of low fluence.

Figure 7. FTIR spectra of the graphene oxide film reduced with high and low fluence.

From FTIR spectra we can make a conclusion that after the graphene oxide reduction with low fluence a number of functional groups still remain in the film. Due to this fact low reduction level is good for the formation of functional composites, where there is a need to couple some nanoparticles, biomolecules or other additives. On the other hand, high reduction level can be used for different applications where a good conductivity is need, for example in flexible electronics, energy storage etc. We can also mention that we showed possibility of manageable graphene oxide reduction for different applications and future formation of functional composite materials.

4. Conclusion
In this work we empirically showed possibility of successful reduction of graphene oxide with relatively low-cost lasers (near IR and blue) and reviewed difference between “ready-to-use” device (commercial laser engraver) with powerful near IR laser and laboratory device, with low power blue laser. Both devices showed possibility of manageable reduction of graphene oxide but blue laser showed significantly less variation and better repeatability, of resistance, that was between 4 to 12 kOhm. This result is from one to 3 order of magnitude lower than in case of laser engraver. We also showed presence of different functional groups, in particular carboxyl, that is important for such application as chemical and biosensor development and functional composites formation.

Acknowledgement
This work is financially supported by Ministry of Science and Higher Education of Russian Federation grant number 14.574.21.0160 (grant unique I.D. RFMEFI57417X0160).

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