

Qualitative analysis of reduction degree in reduced graphene oxide solution by femtosecond laser-induced breakdown spectroscopy

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Abstract: A new approach for the qualitative analysis of reduction degree through the ratio of carbon and oxygen (C:O) in reduced graphene oxide (r-GO) solution by femtosecond laser-induced breakdown spectroscopy (fs-LIBS) was proposed. Firstly, graphene oxide solution was reduced by irradiation with fs laser beams with different energies; subsequently, the carbon and oxygen content was detected through the changes in the intensity of carbon and oxygen obtained by fs-LIBS. The ratio (C:O) and the oxygen content of the observed data by LIBS were associated with the fs laser radiated energies; it was evident that the ratio increased and the oxygen content decreased with the incremented fs laser radiated energies. Fs-LIBS realized online detecting and qualitative analysis of the reduction degree of GO solutions. This method displays a prompt and time-saving way for detecting the reduction degree of r-GO solutions and can promote the applications of r-GO with different reduction degrees.

1. Introduction

Graphene has been regarded as superior to traditional materials due to its excellent mechanical, electrical, thermal, and optical properties, which has also a promising candidate for various applications in next-generation materials and can be produced through the reduction of graphene oxide (GO) [1]. Inexpensive graphite can be processed using cost-effective chemical methods to produce high yields of GO decorated by oxygen-containing groups in the plane. Both these facts indicate that GO is a suitable precursor for the bulk production of graphene-based materials [2]. Therefore, the reduction of GO is undoubtedly a crucial method for preparing graphene [3] and different reduction processes result in different structures, which in turn affect the final properties of the r-GO. For a reduction process, the reduction degree is a key parameter that can be characterized using analytical techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy [4]. However, acquiring reduction information immediately through the aforementioned methods is difficult. Laser-induced breakdown spectroscopy (LIBS), performed through the analysis of optical emission from laser-induced plasma on a target surface, is a rapid, almost nondestructive, remote, and multi-element analysis and is a promising technique for a large range of applications and [5] has been widely applied on diverse materials [6]. However, few publications have focused on using LIBS to observe the degree of reduction from GO solution to r-GO solution.

This paper proposes a novel characterization method to qualitatively detect the reduction degree of GO solution by fs-LIBS. Firstly, equivalent GO solutions were irradiated with fs laser beams of different energies for a specified period of time to remove oxygen-containing groups from GO basal planes in



different degrees [7]. Thereafter, fs-LIBS was used to qualitatively detect the oxygen and carbon content. Samples with higher reduction degree showed lower oxygen intensity. This is a neoteric characterization method to qualitatively probe the reduction degree of GO solution by fs-LIBS and it is more rapid to analyze the reduction of GO solution. Also, the method extends the applied fields of r-GO in storage, electricity and others [8].

2. Experimental methods

2.1. Sample preparation

Colloidal solution of GO with the concentration of 2mg/ml was equally divided into seven copies. Before irradiation, GO solution was agitated in an ultrasonic bath for 30 minutes for exfoliation of GO sheets. To keep homogeneity during laser irradiation, a magnetic stirrer was used and a transparent 1mL-bottle filled with GO aqueous was placed on it. Femtosecond laser fluence was changed from 20 to 70 mJ/cm² with a progressive fluence increment of 10mJ/cm² and all the GO solution was disposed with a constant irradiation time for 1 hour through a plano-convex lens with the focal length of 100mm. The lens position was set at a constant distance about 105mm from the bottom of the colloidal solution to keep the interaction volume in the solution constant. Afterwards, post-irradiation GO solution was also agitated in an ultrasonic bath for 30 minutes to avoid suspension. Finally, the post-irradiation GO solution with different fluences and original GO solution was put onto an aluminum and then dried to form layer samples in a vacuum oven with the drying time of constant 5 hours. The femtosecond laser directly irradiated on the formed GO film to obtain the content of carbon and oxygen [9].

2.2 Experimental setup

Figure 1 schematized the setup of the fs-LIBS system used in this study. A Ti: sapphire laser system with a central wavelength of 800 nm and a pulse duration of 70 fs was used for plasma generation. The maximum repetition frequency of the fs laser was 1kHz. The laser energy was adjusted using a combination of a half-wavelength plate and a polarizer; the pulse energy could be changed from 40μJ to 120μJ with a progressive energy increment of 20μJ. The femtosecond pulse was focused onto the surface of the dried graphene oxide film through a 5×objective (NA=0.15) lens to form a beam spot with a diameter of approximately 6.4μm. Samples were fixed on a mobile three-dimensional platform. Two quartz plano-convex lenses (focal length, 50 mm and 100 mm) were used to collect the emission into a fiber, which was perpendicular to the incident direction of laser and connected to a spectrometer (Shamrock 750, Andor). An intensified charge-coupled device (ICCD) (DH334T-18U-03, Andor, pixel: 1024×1024) was used to detect the spectral lines. To guarantee a fresh ablated surface for each laser shot, laser frequency of 10 Hz was used and the moving speed of platform was set to 0.5 mm/s. The each spectrum was the average spectra of 100 accumulations for a better signal-to-noise ratio. The gate delay and gate width of ICCD detector were 20 ns and 100 ns, respectively. The experiments were carried out in a standard atmosphere.

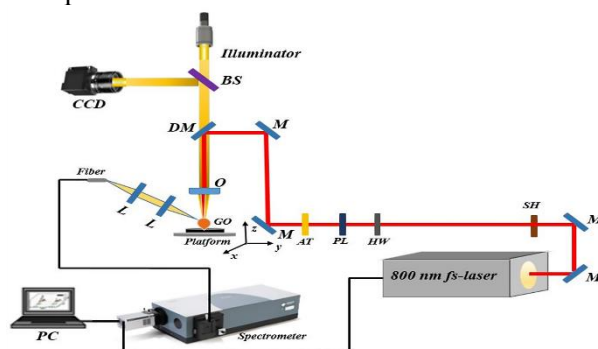


Figure 1 Experimental setup of ultrafast LIBS. (SH: shutter, HW: half-wave plate, PL: polarizer, AT: attenuator, M: mirror.)

3. Results and Discussions

3.1 Graphene oxide spectra under single pulse irradiation

In fs-LIBS, the laser-induced plasma generated by focusing femtosecond laser pulses on the GO and r-GO films exhibited a specific optical response owing to the electronic relaxation of atoms. Atomic emission lines were obtained in a pixel-by-pixel manner by scanning each sample's surface. According to the atomic spectrum database of the National Institute for Standards and Technology, the C atomic line appearing at 786nm and O atomic line appearing at 777nm were prominent to characterize the intensity of the spectrum which can also be used to illustrate the reduction degree. The spectroscopic data of selected atomic lines were extracted from the NIST database and were listed in table 1. Figure 2 showed the emission spectra of original GO film produced by single-pulse fs-LIBS covering the reference spectral range with the characteristic emission lines of atomic species (C and O) in the spectra. A laser fluence of 180 J/cm^2 and 100 accumulations was used to preferably distinguish specific spectral lines. The prominent atomic peaks in the spectra were observed at 786.6626nm for C I transitions and 777.3104nm for O transitions.

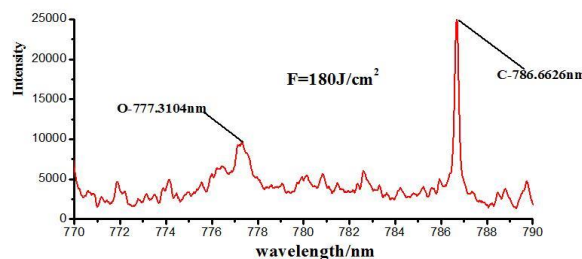


Figure 2 Emission spectra in air produced by fs-LIBS with the characteristic emission lines in the spectra

Table 1 Specific atomic lines that appeared in the spectra

Wavelength, $\lambda_{ij}(\text{nm})$	Transition probability, $A_{ij}(10^8 \text{ s}^{-1})$	Lower energy level, $E_i(\text{eV})$	Upper energy level, $E_j(\text{eV})$
C-786.088	0.0153	8.85066275	10.42745830
O-777.194	0.369	9.1460911	10.7409313

It was generally known that double pulse LIBS generated a better effect on signal enhancement than single pulse in semiconductor and insulator materials. We also explored the spectral signal strength under single pulse and double pulse of different pulse delays. Under the same femtosecond laser fluence, the signal enhancement factor was optimal under the double pulse delay of 120 ps and the ratio was about 1.4 times comparing to single pulse. It was not difficult to find that double pulse had inconspicuous enhancement effect under different pulse delays. Then we adjusted a series of incident laser fluence and chose the optimal pulse delay but the enhancement ratio was still not obvious. The related experimental results were not expressed so the laser detection fluences in this article were used by single pulse.

3.2 LIBS of oxygen content in GO and r-GO

Under different reduction energies, the fs laser was used to dispose these dried films of same conditions, and then detecting the varying signal strength of oxygen and carbon by the method of femtosecond laser induced breakdown spectroscopy corresponding to different reduction degrees. The oxygen spectrum was detected at different fs incident laser fluences, ranging from 120 to 360 J/cm^2 with an increment of 60 J/cm^2 step by step respectively; the corresponding results were depicted in Figure 3. It was distinctly evident that under the same reduction degree, the interaction between laser and materials became violent with the increment of laser fluence which resulted in the enhancement of the plasma temperature and

density as well as the collected spectral intensity of oxygen and carbon correspondingly. Under same fs laser fluences, we definitely draw a conclusion that as the laser reduction energy grew higher, the intensity of oxygen became lower and the degree of reduction increased.

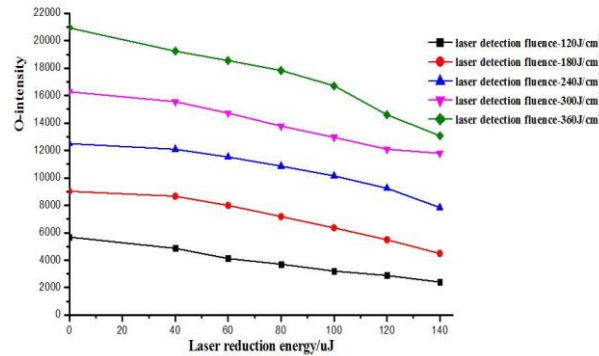


Figure 3. Signal intensities of oxygen in GO film and r-GO film at different fs laser reduction energy levels

Based on the principles of internal standard methods, the spectral signal intensity of elemental carbon in same spectral region was also detected to eliminate the influence of external factors, including laser power stability, beam quality difference, and vibration of experimental translational motion. Thus, the signal intensities of carbon and oxygen under different femtosecond laser detection fluences and reduction energies were obtained, and the change in the intensity of oxygen was explored through the spectral line intensity ratio of carbon and oxygen during the reduction process, as shown in Fig. 4. At the same femtosecond laser detection fluence, the degree of elimination of oxygen functional groups increased with the increase of reduction energy; the ratio increased correspondingly. At the same laser reduction energy, the signal intensity ratio of carbon and oxygen increased with the increase of the femtosecond laser detection fluence. It was evident that as the laser fluence increased, the increasing trend gradually became negligible. This finding may be explained as the attenuated degree of carbon was weaker than oxygen under higher laser detection fluences.

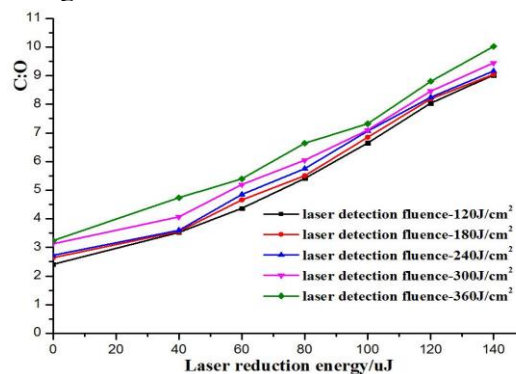


Figure 4. Signal intensity ratio of carbon and oxygen in GO and r-GO of different femtosecond laser energy levels

Then we chose three representative laser fluences of 120、180 and 240 J/cm² to make the fitting curves of the relationship between the signal intensity ratio of carbon and oxygen and the laser reduction energy, which were defined as a variable and a dependent variable, respectively. Figure 5、figure 6 and figure 7 show the fitting curves of the relationship and we can acquire the linear expressions of 120(1)、180 (2) and 240 J/cm²(3) as follows:

$$Y_{ratio} = 0.09864X_{reduction-energy} + 1.82859 \quad (1)$$

$$Y_{ratio} = 0.09753X_{reduction-energy} + 2.15364 \quad (2)$$

$$Y_{ratio} = 0.09948X_{reduction-energy} + 2.68614 \quad (3)$$

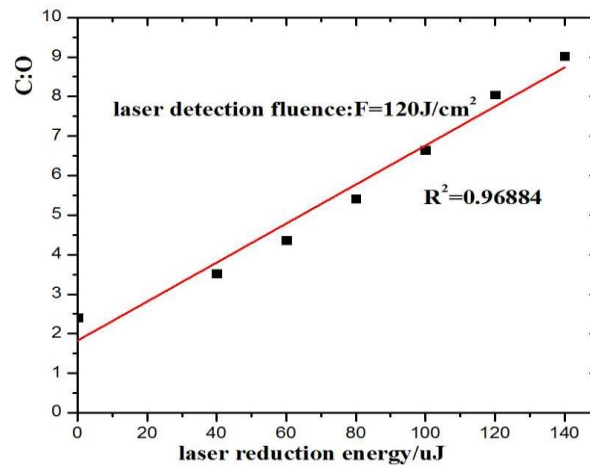


Figure 5. Fitting curves of the relationship between the signal intensity ratio of carbon and oxygen and the laser reduction energy under different fs-laser detection fluence: 120 J/cm²

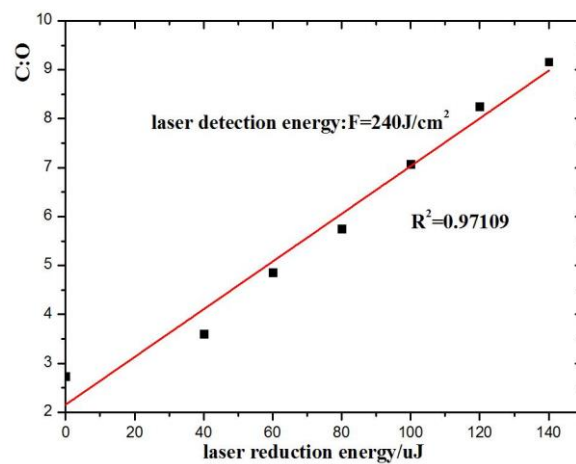


Figure 6. Fitting curves of the relationship between the signal intensity ratio of carbon and oxygen and the laser reduction energy under different fs-laser detection fluence: 240 J/cm²

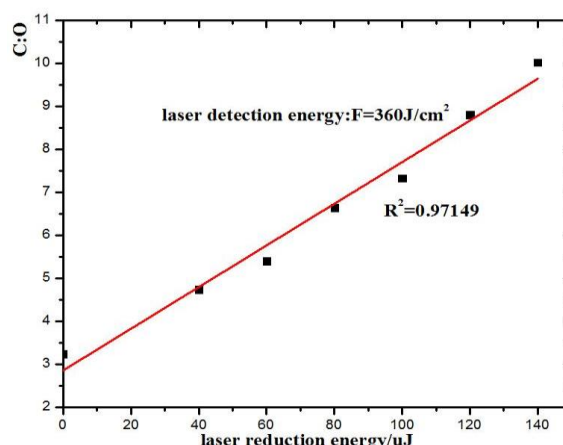


Figure 7. Fitting curves of the relationship between the signal intensity ratio of carbon and oxygen and the laser reduction energy under different fs-laser detection fluence: 360 J/cm^2

Comparing the aforementioned figures, we could easily draw a conclusion that the fitting errors were mostly ignored and the slopes of the fitting curves under different laser detection fluences were approximately similar. In a word, we put forward a new kind of qualitative detection method to detect the reduction degree of graphene oxide and the repeatability under different incident laser fluences was considerable. In other words, different incident laser fluences had a negligible influence on qualitative detection of the reduction degree. It can be indicated that the method provided a neoteric, convenient and time-saving way for detecting the reduction degree of GO solutions.

4. Conclusion

Currently, research on reducing GO to graphene features is attracting considerable scholarly attention and various means are available for reducing GO and then detect the reduction of GO. In this paper, the GO solutions were irradiated with an fs-laser with different laser energy [10]. We evaluated the reduction of GO to r-GO using a novel characterization method based on fs-LIBS. The reduction degree of GO was determined by measuring the spectrum intensity ratio of oxygen and carbon. We found that different incident laser fluences had a negligible influence on qualitative detection of the reduction degree and the repeatability under different incident laser fluences was considerable. It can be considered as a crucial technology for nondestructive and real-time detection, which not only saves considerable time, but also facilitates the scientific applications of GO with different reduction degrees [11].

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