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Experimental investigation of the effects of different liquid environments on the graphene oxide produced by laser ablation method

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ABSTRACT

In this work, the effects of liquid environments on the characteristics and optical properties of carbon nanostructures – in particular, Graphene Oxide (GO) – prepared by pulsed laser ablation were studied experimentally. The second harmonic beam of a Q-switched Nd:YAG laser of 532 nm wavelength at 6 ns pulse width and 0.7 J/cm^2 fluence was employed to irradiate the graphite target in liquid nitrogen, deionized water, and 0.01 M CTAB solution under the same initial experimental conditions. Produced nanostructures were characterized by Raman scattering spectrum, FE-SEM and TEM images, Photoluminescence, and UV–Vis-NIR spectrum. TEM and FE-SEM images show sheet-like morphology with few square micrometer area graphenes in all samples. Raman and UV–Vis-NIR analyses show that graphene is oxidized due to the presence of oxygen molecules in ablation environment. Results demonstrate that the graphene nanosheets produced in deionized water are multilayer, contains the largest sp^2 domain size, the least defects and the lowest possibility of aggregation.

1. Introduction

Graphene is a single sheet of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice [1]. It can be stacked into three-dimensional graphite, rolled into one-dimensional nanotubes, or wrapped into zero-dimensional fullerenes [2,3]. Graphene has been receiving a growing attention from diverse research fields due to its unique electrical, optical, and mechanical properties [4]. A perfect single-layered graphene sheet, in which every carbon atom is sp^2 hybridized and π-conjugated with adjacent carbons, is a zero band gap semiconductor and not expected to be photoactive or photoluminescent [5]. By contrast, some of the reports show that chemically synthesized Graphene Oxide (GO) exhibits a broad photoluminescence where the electronic structure has been modified [6]. The oxidation of graphene causes the formation of graphitic islands in GO which produces a distribution of the π-network and thus opens up a band gap in the electronic structure [7]. The band gap of GO can be tunable by varying the oxidation level [8]. In GO, large fraction (0.5–0.6) of carbon is sp^3 hybridized and is covalently bonded with oxygen in a form of epoxy and hydroxyl groups [9,10]. The remaining carbon is sp^2 hybridized and are bonded either with neighboring carbon atoms or with oxygen in the form of carboxyl and carbonyl groups, which predominantly decorate the edges of the graphene sheets. Therefore, GO is a two dimensional network of sp^2 and sp^3 bonded atoms, in contrast to an ideal graphene sheet which consists of 100% sp^2 hybridized carbon atoms. This unique atomic and electronic structure of GO, consisting of variable sp^2/sp^3 fractions, opens up possibilities for new functionalities [6]. In the method which was used in this article, there is lots of oxygen molecules in the ablation environment, lead to oxidation carbon molecules during the production of graphene.

Graphene can be synthesized by various methods such as chemical vapor deposition, mechanical exfoliation and cleavage, and annealing a single-crystal SiC under ultrahigh vacuum [11,12]. Other graphene preparation methods are based on unzipping of nanotubes [13] and chemical or electro chemical reduction of exfoliated graphite oxide [14]. These methods, however, have many disadvantages including high energy requirement, low yield, limitation of instrument [11,12] and difficulty to control the size [15]. Furthermore the chemical by products in these methods may be harmful for environment and graphene derived by these methods could contain a significant amount of oxygen functional groups and defects [11,12].

Pulsed laser ablation (PLA) of graphite target in liquid environment is another method for producing graphene [16]. The PLA technique possesses the advantages of simplicity of the procedure and inexpensive equipment for controlling the ablation atmosphere [17]. Laser wavelength, pulse width, spot size, intensity,

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temperature, as well as the ablation liquid environment are strong tools to control the final production of laser ablation process [15,18]. Changes in the liquid environment used in laser ablation provide a simple and flexible technique to modify the properties of nanostructures [19]. Laser energy may break the weak Van der Waals bonds between the graphite sheets to produce graphene. Beside graphene nanosheets we have different forms of carbonic nanoparticles in the liquid environment.

There have been many efforts on investigating the effects of laser parameter such as wavelength, pulse width, or fluence on the properties of laser produced graphene. Recently, Mortazavi et al. have presented a work on the fabrication of graphene with a Q-switched Nd:YAG laser ablation of graphite target in liquid nitrogen [16]. Sadeghi et al. [20] investigated the effects of liquid environment on the optical properties of produced graphene. They used the fundamental wavelength of Nd:YAG laser to produced graphene. Tabatabaie et al. [15] studied the effect of laser fluence on the characteristics of produced graphene in liquid nitrogen. In this experimental research for the first time we have investigated the effects of liquid environments on the characteristics of carbon nanostructures produced by 532 nm wavelength laser pulse. Liquid nitrogen, deionized water, and 0.01 M CTAB were used as the ablation liquid environments. Aim of this work is to investigate the potential of different liquid environments to produce graphene nanosheets and demonstrate the effect of surrounding molecules on them. Liquid nitrogen is a nonpolar liquid, water is polar liquid, and CTAB is a cationic surfactant. Moreover, the density of liquid environments was reduced in 0.01 M CTAB, water, and liquid nitrogen, respectively. Details about the densities are presented in Table 1. Different natures of these liquids as well as their different density are effective topics to influence the formation of different sized nanostructures. Rate of nanostructures production by laser ablation method is strongly under the influence of ablation liquid environment. Density of the liquid may change the pressure of plasma plume which forms on the surface of target during the ablation process and the shock waves which propagate in the target, lead to change the amount of nanostructures which ablate from the surface of target.

2. Experimental setup

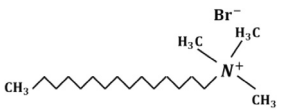
Carbon nanoparticles and graphene oxide were produced by pulsed laser ablation of a graphite plate (99.9%) in various liquid environments. A graphite plate was placed on the bottom of an open glass cylindrical vessel filled with 80 mL of liquid and height of the liquid on the surface of the target was 5 mm. All equipment include the graphite plate was cleaned ultrasonically in ethanol, acetone and deionized water before the experiments. Graphite target was ablated with the second harmonic pulse of Nd:YAG laser, operated at 7 ns pulse width and 5 Hz repetition rate and 532 nm wavelength. 5000 laser pulses were used to produce carbon nanostructures in various liquid environments. The fluence of laser pulse was 0.7 J/cm^2 with 6 mm diameter. Output of laser was focused on the surface of graphite target using a 100 mm focal length convex lens. Using $w_{02} \cong \lambda f/\pi w_{01}$, the spot size of laser pulse on the surface of target was calculated to be about 30 μm. In this equation w_{01} and w_{02} are the initial size of the beam and spot size respectively. λ is the laser wavelength and f is the focal distance of the lens. During laser ablation, the target was rotated manually to ensure uniform ablation and to avoid a texturing effect.

We have produced carbon nanostructures and graphene oxide in liquid nitrogen, deionized water, and cetyltrimethylammonium bromide (CTAB) 0.01 M. Detail about the samples preparation is presented in Table 1. For preparation of carbon nanostructure in liquid nitrogen, the cylindrical vessel was full of liquid nitrogen as the media for pulsed laser ablation. Height of liquid nitrogen on the target was 0.5 cm. The injection of liquid nitrogen into cylindrical vessel successively continues during the time that a thermal steady state condition is obtained. After laser exposure, the residual liquid nitrogen has evaporated at the room temperature and immediately deionized water was added to the cylindrical vessel establishing a suspension for the carbon nanostructure.

A variety of analytical techniques were applied for the characterization of products. The optical properties of the samples were examined at room temperature by UV–Vis-NIR spectrophotometer from PG instruments Ltd. To record the spectra, samples were in a 10 mm path length quartz cells with reference to correspond solution. Transmission electron microscope (TEM), from Zeiss EM10C was conducted by placing a drop of the concentrated suspension on a carbon coated copper grid. Their morphology was investigated by Hitachi S4160 field emission scanning electron microscope (FE-SEM). Raman Thermo Nicolet disperse spectroscope from Almega was utilized to determine the structure, quality and amount of GO in dried drops of suspensions on glass substrate with 0.1 cm^{-1} spectral resolution. Room-temperature photoluminescence

Fig. 1. Carbon nanostructures produced by pulsed laser ablation in liquid nitrogen, deionized water and 0.01 M CTAB.

Table 1
Liquid environment, density, wavelength of absorption peak, and bandgap energy of samples produced by PLA.

Sample	1	2	3
Liquid environment	Liquid nitrogen	Deionized water	CTAB 0.01 M
Molecule structure	$N \equiv N$		
Density (g/ml)	0.8064	1.0028	1.0073
Wavelength of absorption peak (nm)	304	306.5	308.5
Direct bandgap energy (eV)	3.9	3.4	3.1