Materials Chemistry and Physics 203 (2018) 235–242

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Effects of CTAB concentration on the quality of graphene oxide nanosheets produced by green laser ablation

Elnaz Vaghri, Davoud Dorranian*, Mahmood Ghoranneviss

Laser Lab., Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran

HIGHLIGHTS

- Graphene oxide nanosheets are successfully produced by pulsed laser ablation method.
- CTAB solutions with different concentrations were used as the solvent.
- Graphene oxide nano sheets with sheet-like structures characterized by SEM and TEM.

ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form
16 September 2017
Accepted 6 October 2017
Available online 9 October 2017

Keywords:
Pulsed laser ablation
Graphene oxide
Cetyl trimethyl ammonium bromide
Graphite
Photoluminescence
TEM

ABSTRACT

In this study the influence of the concentration level of cetyl trimethyl ammonium bromide (CTAB) as the ablation environmental medium on the characteristics of graphene oxide nanosheets, produced by laser ablation method has been surveyed. The second harmonic of a Q-switched Nd:YAG laser at 532 nm wavelength and 7 ns pulse width and 0.5 J/cm^2 fluence was used to irradiate a graphite plate in CTAB solution. The produced samples were characterized by field emission scanning electron microscopy (FE-SEM), UV–Vis–NIR absorption spectroscopy, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Raman and photoluminescence (PL) spectroscopy. Raman results exhibit that the 0.04 M concentration of CTAB is the optimum concentration for producing high-quality graphene oxide nanosheets. The experimental results suggest that the amount of defects and the number of graphene oxide layers can be changed with adjusting the concentration level of CTAB in suspensions. This paper can be beneficial guidance to produce of high-quality graphene oxide nanosheets.

1. Introduction

Since the first appearance of graphene in 2004 [1], graphene structures have evoked a considerable interest throughout both academic and industrial communities owing to their extraordinary properties including: large surface area [2], high electrical conductivity [3], extremely high electron mobility [4], excellent thermal conductivity [5] and etc. These remarkable characteristics enable graphene to be utilized in many technological fields such as batteries [6], supercapacitors [7], sensors [8], solar cells [9], and composites [10]. Graphene is a two-dimensional material formed by a single atomic layer of sp^2 bonded carbon, which is arranged in a honeycomb lattice [11]. In spite of the interesting properties, graphene sheets tend to form irreversible aggregation because of strong π-π stacking interaction and Van der Waals forces between different sheets and it limits their applications [12]. Studies show that applying protective reagents and surfactants such as polystyrene, silicone, octadeyl amine, dodecyl trimethyl ammonium bromide (DTAB), sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) to the graphene surface could partially improve this problem [12–14]. CTAB is a cationic surfactant which contains a cationic polar head and a hydrophobic tail which enables it either to agglomerate negatively charged nanoparticles and to utilize the hydrophobic effect [15]. Among the graphene family, graphite oxide sheets, now named graphene oxide (GO), is the most famous material which basically produces by chemical oxidation and exfoliation of graphite. GO consists of oxygen functional groups on its surface including carbonyl/carboxyl groups at the edges on sp^2 carbon atoms and epoxy/hydroxyl groups on sp^3 hybridized carbon atoms on the basal planes [16]. In GO structure, there are a lot of negatively charged sites resulting from the negative charges of carboxyl groups at the edges of GO nanosheets. When CTAB intercalation in the interlayer of GO nanosheets, the ionic

* Corresponding author.
E-mail address: doran@srbiau.ac.ir (D. Dorranian).

https://doi.org/10.1016/j.matchemphys.2017.10.010
0254-0584/

interaction can occur between the positively charged ammonium ions of CTAB head and the negatively charged carboxyl groups of GO. This phenomenon lessens the GO nanosheets aggregation. Recently, dispersed GO solutions have attracted many scientific attentions to solve problems and improve traditional procedures in technological, and industrial applications due to their outstanding properties such as tremendous adsorption capacity, removal efficiency, facile process, convenient operation, and low cost. For example there have been researches about using aqueous GO suspensions in adsorbing and removing organic contaminants from waste water [17], oxidation of alcohols and *cis*-stilbene and hydration of various alkynes to the corresponding aldehydes, acids and ketones under mild conditions [18,19]. Furthermore, interesting applications of GO are found and studied in various fields of technology such as optoelectronics, supercapacitors [20], memory devices, composite materials, cellular imaging [21], electrical biosensing [22], gas sensors [23], drug delivery agents [11], and solar cells [24], and developing researches are being actively pursued. Also, the liquid crystalline behavior of GO has enabled the design of facile and effective solution processing methods for assembling highly ordered macroscopic graphene structures, further expanding the development of novel graphene-based devices [25]. There are several reports on producing GO in CTAB medium. Mao and co-workers synthesized CTAB-functionalized graphene nanosheets and used it as the modified material on electrode to determine Sudan I; also they find that the electrochemical response of Sudan I remarkably increased compared to glassy carbon electrode [26]. Fan et al. synthesized CTAB-intercalated graphene/polypyrrole nanocomposites via in situ oxidative polymerization [27]. Their results show that the better electrical conductivities achieved by more amount of CGN in the nanocomposites. Li et al. fabricated graphene oxide–Au nanoparticle hybrids [28]. They found that the existence of CTAB in the GO–AuNR substrate greatly improves the electronic transition efficiency and surface-enhanced Raman scattering (SERS) ability. Das and co-workers describes that the presence of GO in CTAB reverse micelles led to the development of self-assembled soft nanocomposites which is beneficial for improving efficiency of surface-active enzymes [29]. To produce graphene and its derivatives, a wide variety of methods and processes has been devised including; chemical vapor deposition, chemical exfoliation, epitaxial growth, electrochemical methods, pulsed laser ablation, and other specific techniques. Among these reported methods, pulsed laser ablation (PLA) of a solid target in a confining liquid is a relatively new and efficient technology to prepare various kinds of nanocrystals and nanostructures. Compared to the other techniques, the significant advantages of the PLA method as a one-step process, would be enumerated as; inexpensive equipments to control the ablation atmosphere, the simplicity of the experimental setup and the ability to control the size of synthesized material by changing different parameters such as laser wavelength, pulse laser duration, laser fluency, the pH of the solution, the solution temperature, and etc. [30–33]. Fabbro et al. modeled the laser ablation process in three stages. In the first stage, during the laser heating, the generated pressure is typically pressure is typically 4–10 times greater than the corresponding one obtained in direct ablation. The second stage begins after the switch-off of the laser and is characterized by an adiabatic cooling of the plasma which maintains the applied pressure over a period which is about 2 times the laser-pulse duration. Finally, the third stage concerns also the adiabatic cooling of the recombined plasma, but during this period the exerted pressure is too small to realize a plastic deformation of the material [31,34]. The pressure of the plasma plume on the surface of the target is directly proportional with the ablation liquid environment [31]. Hence, care has to be taken in the control of the concentration of ablation liquid medium to optimize the characteristics of the ablation products. In this paper, the synthesis process of GO is done by laser ablation technique in aqueous environment including different concentrations of CTAB.

2. Experimental details

There are various physical and chemical methods to prepare GO in laboratorial conditions. These methods are principally composed of a carbon based material to be influenced by the expected procedure and an environmental material to make a suitable background that may even share the required oxygen based on the pre-planned oxidation process. It is obvious that varying any of the aforementioned items and conditions would extremely affect the ultimate outcome. In the present investigation, graphite is used as the source of carbon and a suspension of the mixture of the CTAB powder and distilled water (briefly named CTAB solution) is used as the environmental material. In order to obtain various concentrations of the CTAB solutions, first of all the amount of the needed CTAB powder for each desired concentration was calculated, then they were added slowly into 100 ml of distilled water separately and at last to prepare the transparent aqueous solutions, every solution was stirred continuously. During this step, the temperature was kept at 50 °C and the results were the solutions with the predefined concentrations of CTAB. The samples were labeled as S_1, S_2, S_3, S_4 and S_5 relative to their concentration level of CTAB which were designed to be 0.02, 0.04, 0.06, 0.08, and 0.1 M respectively. The formation of the GO nanosheets was carried out using a pulsed nanosecond laser applying on the pure graphite target (with 99.99% purity) by a Q-switched Nd:YAG laser at a wavelength of 532 nm, with a pulse-repetition rate of 5 Hz, a pulse width of 7ns and a pulse fluency of 0.5 J/cm^2 at the room temperature. Before starting the experiment, to remove any residual contaminants, the graphite targets were cleaned ultrasonically in ethanol, acetone and distilled water solutions respectively for 15 min and then each one was placed on the bottom of a glass vessel containing CTAB/water solution. The target was ablated by a laser beam of 6 mm in diameter. Also the laser was focused using a lens with a focal length of 85 mm on the target surface. Height of the aqueous solution on the target was 8 mm. During laser ablation, the target was being moved continuously to achieve a uniform ablation toward the graphite surface. The final sample solutions are pictured in Fig. 1.

In the present study, different analytical techniques have been utilized for the characterization of the samples. UV–Vis–NIR spectrophotometer from PG instruments Ltd in the absorption mode was employed to investigate the optical properties. The bonding structures of the produced samples were characterized by the Fourier transform infrared (FTIR) spectroscopy with a NEXUS 870 FTIR Spectrometer from thermo Nicolet Co in the range of 500–4000 cm^{-1}. Raman measurements were performed using an Almega Thermo Nicolet Dispersive Raman Spectrometer with 532 nm of a Nd:YLF laser. The luminescence properties of the samples were measured at room temperature by photoluminescence (PL) spectrophotometer (Cary Eclips) using a Xe lamp as the light source. Transmission electron microscopy micrographs were obtained using Zeiss-EM10C microscope with an acceleration voltage of 80 KV. In addition, the surface morphology of the samples was evaluated by Hitachi, S-4160 field emission scanning electron microscopy (FE-SEM).

3. Results and discussion

3.1. UV-Vis-NIR absorption spectrum

Fig. 1 indicates the pictures of the sample suspensions. In the laser ablation process of graphite target in liquid medium, various