Applied Surface Science 444 (2018) 578–583

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Laser-induced reduction of graphene oxide powders by high pulsed ultraviolet laser irradiations

Chii-Rong Yang [a], Shih-Feng Tseng [b,*], Yu-Ting Chen [a]

[a] Department of Mechatronic Engineering, National Taiwan Normal University, Taipei 10610, Taiwan
[b] Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

ARTICLE INFO

Article history:
Received 7 February 2018
Revised 7 March 2018
Accepted 11 March 2018
Available online 14 March 2018

Keywords:
Laser-induced reduction
Graphene oxide powders
Raman spectroscopy
X-ray photoelectron spectroscopy
Surface area analyzer

ABSTRACT

This study aims to develop a laser-induced reduction approach for graphene oxide (GO) powders fabricated by using high pulsed ultraviolet laser irradiations. Before and after the laser irradiation with different fluences, the physical and electrical properties of homemade GO powders and reduced graphene oxide (rGO) powders were measured and analyzed using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), surface area analyzer, and four-point probe instrument. The laser irradiation parameters included the pulse repetition frequency of 100 kHz, the scanning speed of galvanometers of 50 mm/s, the number of laser irradiated cycles of 10, and the laser fluences of ranging from 0.153 mJ/cm^2 to 0.525 mJ/cm^2. The laser reduction experiments of GO powders demonstrated that the largest relative intensity of the 2D peak and specific surface area were found at the laser fluence of 0.438 mJ/cm^2. Moreover, the electrical resistance sharply decreased from 280 MΩ in the initial GO powders to 0.267 MΩ in rGO powders at a laser irradiation fluence of 0.438. The C/O ratio was increased from 0.232 in the initial GO powders to 1.86 in the rGO powders at a laser irradiation fluence of 0.525 mJ/cm^2; furthermore, the C/O ratios increased with increasing the laser fluences.

1. Introduction

Graphene is a two-dimensional and hexagonal lattice material with a single atomic layer or few atomic layers. Due to its high room-temperature carrier mobility of up to 2×10^5 cm^2/Vs [1,2], high thermal conductivity of 5300 W/mK [3,4], high optical transmittance of more than 90% [5–7], and high mechanical strength with Young's modulus of 1 TPa [8,9], graphene materials have widely promising applications in solar cells, light-emitting diodes (LEDs), touch-screen panels, energy storage devices, single molecule gas detection, and other transparent electrodes [10–14]. Various approaches of manufacturing graphene materials include chemical vapor deposition (CVD), micromechanical cleavage of highly oriented pyrolytic graphite (HOPG), electrochemical exfoliation of HOPG, chemical exfoliation, photo exfoliation, epitaxial growth method, reduction of graphene oxide (GO), and so on [15–18]. Recently, several methods of thermal and electrical reduction of GO to graphene for mass production have been proposed. Trusovas et al. [19] used a picoseconds pulsed laser (wavelength of 1064 nm) processing system combined with a galvanometric scanner to reduce graphite oxide to graphene. After the laser irradiation on graphite oxide films with the laser power of 50 mW and the scanning speed of 30 mm/s, the largest relative intensity of 2D-peak (2656 cm^{-1}) and the minimum structural defects of D-peak (1331 cm^{-1}) of reduced graphite oxide films were clearly observed by a Raman spectroscopy. The experimental and analytic results revealed that a single laser pulse with a fluence of 0.04 J/cm^2 (50 mW) of local temperature increased up to 1400 °C for a few nanoseconds that can sufficient and effective reduction of graphite oxide to graphene by using laser irradiation. Ghadim et al. [20] reported the reduction of GO sheets in the ammonia solution at room temperature by an Nd:YAG pulsed laser system with a wavelength of 532 nm and a average power of 0.3 W. After laser irradiation of 10 min, the 2D-peak (2680 cm^{-1}) of reduced graphene oxide (rGO) sheets was slightly higher than GO ones measured by the Raman spectroscopy. A calculated 2D/G intensity ratio (I_{2D}/I_G) of rGO sheets was 0.038 that had no significant interaction for the pulsed laser reduced sheets in the ammonia solution. By using X-ray photoelectron spectroscopy (XPS) analysis, an oxygen/carbon atomic ratio (O/C) of GO sheets reduced from 49% down to 21% after laser irradiation of 10 min. Teoh et al. [21] presented a versatile technique to reduce three dimensional (3D) GO with micropatterned multilayered structures by the focused laser

* Corresponding author.
E-mail address: tsf@ntut.edu.tw (S.-F. Tseng).

https://doi.org/10.1016/j.apsusc.2018.03.090
0169-4332/

beam (wavelength of 532 nm) irradiation and hierarchical control method. Petridis et al. [22] reported on the development of a KrF excimer pulsed laser (wavelength of 248 nm) induced reduction method for the photoreduction of GO field effect transistors (FETs). To irradiate GO FETs with a laser fluence of 80 mJ/cm^2, the electrical conductivity increased with increasing the laser pulse numbers. The O/C ratio was reduced from 61% in the initial GO to 16% in rGO treated by 120 laser pulses at the fluence 80 mJ/cm^2. Zhou et al. [23] proposed an electrochemical method to produce rGO films with an O/C ratio of less than 6.26%. Moreover, this method combined with a spray-coating technique could accomplish the controllable synthesis of large-area and patterned rGO films with thickness ranging from a single atomic layer to several microns coated on various substrate surfaces, such as flexible plastic, glass, Au, glassy carbon (GC), and indium tin oxide (ITO).

In this study, we used the improved Hummers' method to prepare GO powders. To obtain the reduction of GO powders with a fast, convenient, environmentally friendly, and efficient method, this study focused on the development of a laser-induced reduction technique using an ultraviolet (UV) laser-induced reduction apparatus combined with a high-speed galvanometric scanner. The laser-induced reduction parameters consisted of laser fluences, pulse repetition frequencies, scan speeds of the galvanometric scanner, and number of irradiated cycles. Before and after the laser irradiation with different processing parameters, the Raman spectra, O/C ratio, and specific surface area of GO and rGO powders were observed and analyzed using the Raman spectroscopy, XPS, and surface area analyzer. Moreover, the electrical resistances of GO and rGO powders were measured using a four-point probe instrument.

2. Experimental

2.1. Preparation of GO powders

The homemade GO powders were fabricated by using pre-oxidized, improved Hummers' method, and post-treatment procedures. In the pre-oxidized process, 3 g graphite flakes were dissolved in a solution containing 180 mL H_2SO_4 and heated to 80 °C for 4.5 h to promote the oxidation of the graphite. Then, the graphite oxides were exfoliated using an ultrasonic atomizer for 2 h. The pre-oxidized graphite flakes were obtained using the qualitative filter papers with hole diameter of 1 μm to filter the micro flakes and using a hotplate with 100 °C to dry flakes. Depending on the improved Hummers' method, 360 mL H_2SO_4 was added slowly to the 40 mL H_3PO_4 as a mixture. Afterward 3 g pre-oxidized graphite flakes were added to the mixture, which was cooled to 0 °C in an ice bath for 30 min. Finally, 18 g $KMnO_4$ was added slowly to the mixture and stirred for 1 h. Moreover, the mixture was heated to 50 °C and stirred for 12 h. Then, the mixture was cooled to room temperature, and 30 wt% H_2O_2 was added slowly into the mixture. The completely reacted mixture was a graphene oxide suspension. Fig. 1 shows digital pictures of graphene oxide suspensions with concentration of 0.4 mg/ml (a) and 1 mg/ml (b) created by GO powders dispersed in 100 ml of deionized water.

In the post-treatment process, 1000 mL HCl (10 wt%) was added to the graphene oxide suspension and stirred for 2 h. To remove the supernatants, the GO suspension was centrifuged at 6000 rpm for 30 min. After removing completely metal ions (i.e. Mn and K ions), the GO flakes were washed in distillate water and centrifuged at 6000 rpm for 2 h. The filtered GO flakes were dried in a vacuum oven at 60 °C for 24 h. The GO powders with a diameter of 200 μm were fabricated using a ball grinding mill with zirconia balls of 2 mm diameter for 72 h.

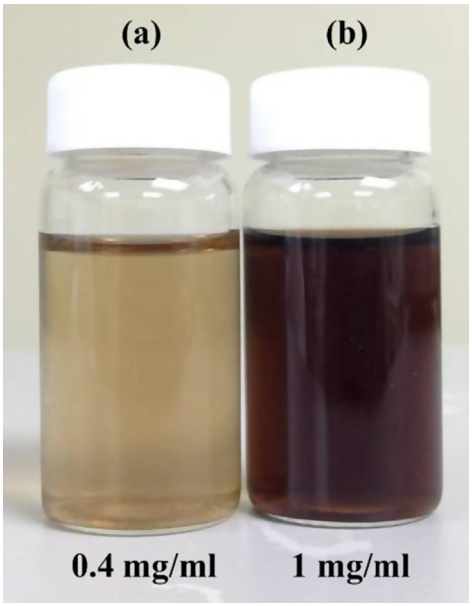

Fig. 1. Digital pictures of graphene oxide suspensions with concentration of 0.4 mg/ml (a) and 1 mg/ml (b) created by GO powders dispersed in 100 ml of deionized water.

2.2. UV laser-induced reduction apparatus and method

GO powders were reduced using the UV pulsed laser (Model: AVIA 355-14, Coherent Inc., USA) working at the 355 nm wengthlength. The specifications of UV laser were following: the laser beam diameter at the exit port of 3.5 mm, the maximal pulse repetition frequency of 300 kHz, the maximal power of 14 W, and the pulse width of 28 ns at the pulse repetition frequency of 100 kHz. Experimental apparatus included a UV laser source, three reflective mirrors, a beam expander with 2 times magnification, a galvanometric scanner with a telecentric lens of 110 mm focusing length and of 60 mm × 60 mm field size, and an XYZ-axes movable stage with ball-screw mechanism, as shown in Fig. 2. The GO powders were placed inside a quartz tube. The laser beam was directly focused through the quartz tube due to the quartz material with high transmittance at the 355 nm waveband.

The laser processing conditions for the irradiated GO powders were carried out as following. The defocused laser beam away from the focused point of 20 mm was irradiated towards GO powder surfaces to avoid damaging and burning those powders with high laser fluences. The defocused spot diameter (D) was approximately 5 mm. The incident laser fluence (F) in J/cm^2 could be calculated by the following equation:

$$F = \frac{E}{A} \tag{1}$$

where E is the laser pulse energy, and A is the area of laser spots. The laser fluences were adjusted from 0.153 mJ/cm^2 to 0.525 mJ/cm^2 for this study. Moreover, the GO powders were reduced by scanning laser beams with a cross line of the laser processing path in X and Y directions of equal line-scan space of 20 μm. Fig. 3 shows schematically the laser irradiation paths. The overlapping rates (O_R) of the laser spot could be defined and estimated as follows [24].

$$O_R = \left(1 - \frac{V}{P_{RF} \times D}\right) \times 100\% \tag{2}$$

where D, V, and P_{RF} are the laser spot diameter, the scanning speed of galvanometers, and the laser pulse repetition rate, respectively. During the tests, the pulse repetition frequencies, scan speeds of