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Influence of laser wavelength on two-dimensional carbon nanosheet formation from laser-induced exfoliation of naphthalene

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ABSTRACT

Pulsed Nd:YAG (532 nm) and Excimer (248 nm) lasers were employed to produce freestanding, two-dimensional (2D), carbon nanosheets (CNSs) from naphthalene, through laser-induced exfoliation. The polymer-to-carbon transition was investigated in terms of laser wavelengths, fluences, as well as target preparations. Continuous and porous CNSs of several nanometers in thickness and micrometers in size were obtained from 532 and 248 nm pulsed laser exfoliation of spin-coated naphthalene films, respectively. The porous morphology is ascribed to the photon-induced dissociation of chemical bonds dominated in 248 nm laser interaction with ablated naphthalene. With the increase of laser fluences from 1 to 5 J cm^{-2}, amorphous carbon and ultrathin CNS structures were obtained in sequence. This work revealed a general mechanism of producing 2D structured carbon materials from pulsed laser exfoliation.

1. Introduction

Two-dimensional (2D) carbon materials have inspired numerous investigation since the discovery of graphene in 2004, for their unique atomic structures and properties [1–3]. Mechanical exfoliation has been firstly employed for producing pristine 2D material [1]. However, organic residue from the scotch tape would leave on sample surface, which needs further thermal annealing [4]. Chemical exfoliation introduces oxidation and reduction of materials, which create defects on sample surfaces [5,6]. Pulsed laser exfoliation has been experimentally demonstrated for producing 2D carbon materials from polymer in 2011 [7]. The spin-coated polymer was put into a vacuum chamber as target. The pulsed 532 nm Nd:YAG laser was introduced to the target surface, and sheet structures were exfoliated. After going through the high temperature process in laser plume, the exfoliated material lands on substrate as 2D carbon nanosheet (CNS). Following studies have been focused on exploring more materials for laser exfoliation into 2D structures [8]. Few-layer graphene has been exfoliated from highly ordered pyrolytic graphite by a pulsed 532 nm Nd:YAG laser. It suggests the formation of 2D carbon structures by pulsed laser exfoliation generally requires a non-oxidation environment, a flat target surface, a laser photon energy lower than the C—C bond energy, and an appropriate ablation depth. In these studies, vacuum chambers were employed to provide the non-oxidation environment.

To simplify the experimental setup, several studies focused on liquid-phase pulsed laser exfoliation of 2D carbon structures in liquid [9–12]. Various solutions, such as N-methyl-pyrrolidone, liquid nitrogen, deionized water, were used to isolate the target materials from oxidation. The laser-induced exfoliations of graphite in water or liquid nitrogen have been demonstrated by pulsed 532 or 1064 nm Nd:YAG lasers [9–11]. The water or liquid nitrogen protects the ablated few-layer graphene sheets from being oxidized by air. The 532 and 1064 nm Nd:YAG lasers provide photons with energies of 2.33 and 1.17 eV, which are lower than most bond energies in polymer and graphite. In comparison with 7 and 10 ns duration time and 5 Hz laser repetitions of 532 and 1064 nm Nd:YAG lasers, femtosecond laser offers a shorter duration time of 35 fs, a higher repetition of 1 kHz, and a photon energy of 1.55 eV corresponding to a laser wavelength of 800 nm [12]. The femtosecond laser interaction with graphite in water results in porous graphene, which is proposed as the reaction between carbon and radicals, where radicals come from the laser-induced water breakdown. The water introduces a sophisticated system for detecting the formation mechanism of porous structure [13].

Pulsed laser exfoliation for 2D materials has shown novel phenomena, however mechanism has been still under investigation. Laser-induced exfoliation, photo-thermal, and photo-chemical processes are taken into consideration. Theoretic studies show simulation results of the possible evolution, where laser wavelength and laser energy were taken into major consideration [14–16].

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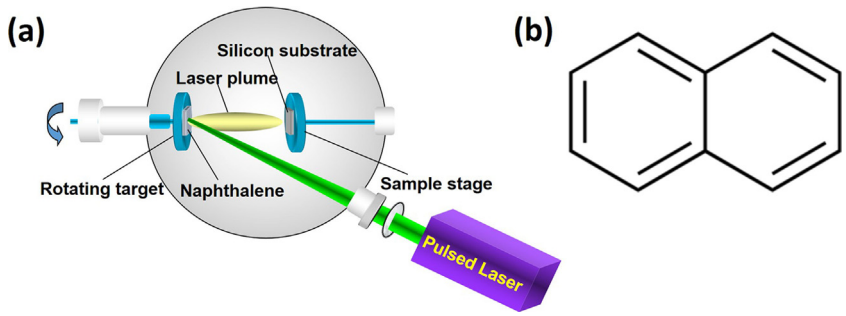

Fig. 1. (a) Schematic diagram of the experimental setup (b) Structural formula of naphthalene.

However, there are few systematic experimental study of laser wavelength and fluence influences on the formation of 2D carbon structures by laser exfoliation. This work was based on pulsed laser interaction with naphthalene, an aromatic hydrocarbon consisting of a fused pair of benzene rings. The target preparation, laser wavelength, and laser fluence were investigated for detecting the mechanism of pulsed laser interaction for 2D materials.

2. Experimental details

2.1. Preparation of naphthalene targets

The white naphthalene powder was dissolved in tetrahydrofuran (THF) by ultrasonication for 20 min, to form a uniformly-dispersed transparent solution with a concentration of 50 g l^{-1}. Subsequently, the polymer solution was applied on 1 cm × 1 cm silicon (Si) (100) wafers by spin coating at a speed of 800 rpm for 30 s. Naphthalene films were obtained and subjected to an elevated temperature at 80 °C for 20 min to evaporate the THF. For comparison, a pressed naphthalene target was prepared with a diameter of 10 mm and a thickness of 5 mm.

2.2. Pulsed laser interaction with naphthalene targets

The experimental setup of the pulsed laser interaction with material is shown in Fig. 1(a). After loaded with the target and one bare silicon wafer as substrate, the chamber was vacuumed to a base pressure of 10^{-5} Torr. Pulsed Nd:YAG (Continuum Powerlite™ Precision II DLS 8010, wavelength = 532 nm, τ = 7 ns) and Excimer (Lambda Physik Compex 205 KrF excimer laser, wavelength = 248 nm, τ = 23 ns) lasers with repetition rates of 1 Hz were used as the irradiation sources. The pulsed laser was focused and introduced into the chamber through a quartz window and interacted with the target. A bare silicon wafer placed 5 cm away from the target was used as the substrate for collecting product. The focused laser beam was around 1 mm in diameter and irradiated the target at an incident angle of 45°. The target was rotating at 50 rpm. The 1 Hz laser was introduced to a fresh target surface spot for each pulse. A few laser pulses (6–8) were applied to the target for a certain laser fluence. All experiments were carried out at room temperature. Laser fluences in a range, from 1 to 5 J cm^{-2}, were used to investigate the pulsed-laser-induced polymer-to-carbon transition process. Higher laser fluence would create caves on silicon wafers.

2.3. Characterization

The products landed on silicon wafers were characterized by a scanning electron microscope (SEM, Hitachi S-4700), a high resolution transmission electron microscope (HRTEM, FEI Tecnai T12), an atomic force microscope (AFM, Veeco DI-3100), and a micro-Raman spectrometer (Renishaw inVia, excitation wavelength of 514 nm).

3. Results and discussion

As shown in Fig. 1(b), the chemical structure of naphthalene consists of the fusion of a pair of benzene rings. Raman spectrum of naphthalene in Fig. 2(a) shows some major peaks at 1382, 1464, 1577, and 3056 cm^{-1}. There are some weak Raman peaks of naphthalene as shown in the inset of Fig. 2(a)–(c). The Raman spectrum and peaks of naphthalene are consistent with previous reports [17–19]. The Raman peaks at 1147, 1382, 1464, 1577, 3005, and 3056 cm^{-1} are related to A_g vibration modes. The Raman peaks at 1245 and 1629 cm^{-1} are related to B_{3g} modes [17–19].

Fig. 3 shows the SEM images of products on the silicon wafers after Nd:YAG laser interaction with spin-coated naphthalene target. When laser fluence is as low as 1 J cm^{-2}, the products on silicon substrate show amorphous structure, as shown in Fig. 3(a). Sheet structures up to several micrometers in size are shown on bare silicon substrates with laser fluences between 2 and 5 J cm^{-2}, as shown in Figs. 3(b) and (c). At 1 J cm^{-2}, the Raman spectrum of amorphous structure reveals clear D and G bands around 1358 and 1580 cm^{-1}, as well as a strong luminescence, indicating a transition state from

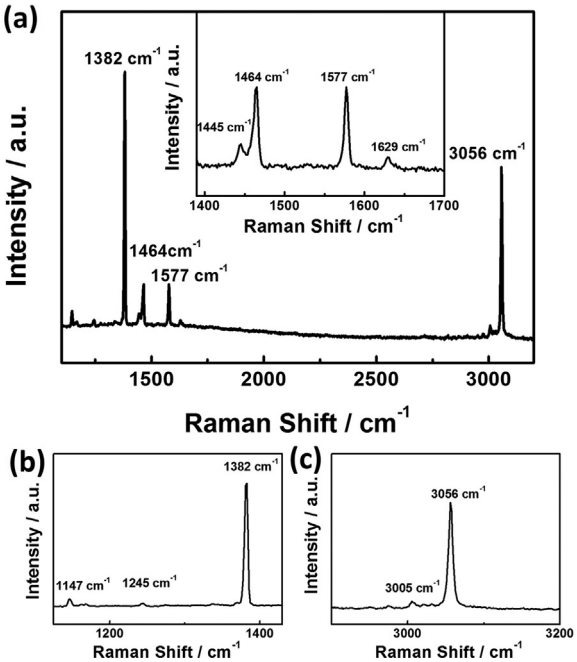

Fig. 2. (a) Raman Spectrum of naphthalene, with inset of the zoomed-in Raman spectrum between 1400 and 1700 cm^{-1}. (b) Zoomed-in Raman spectrum of naphthalene between 1100 and 1450 cm^{-1}. (c) Zoomed-in Raman spectrum of naphthalene between 2900 and 3200 cm^{-1}.