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Preparation of large-size graphene oxide-like with hydroxyl groups and its optoelectronic properties

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ABSTRACT

Laser materials are very important for fabricating laser devices. In this paper, a new type of graphene oxide-like with hydroxyl groups (GOLH) was synthesized for developing pulse laser devices. GOLH was characterized by fourier transform infrared, X-ray diffraction, elemental analysis, scanning electron microscopy, Raman spectra and dynamic light scattering. Experimental results showed that GOLH contained mainly one kind of substituent, hydroxyl group. Average size of GOLH was about 1.5 μm. Its optoelectronic properties were studied by a Q-switched pulse laser. Experimental results suggested that GOLH would be employed as a saturable absorber. A Q-switched pulse laser with the GOLH materials exhibited stable signal intensity and narrow pulse duration, 0.8 μs. Therefore, GOLH would be potential pulse laser materials.

1. Introduction

Laser materials are very important for fabricating laser devices, which have been applied in information, medicine, industry and so on [1]. Laser materials, such as crystal, ceramic, films, nano particles, metal salts and oxides, have been developed to improve properties of laser devices [2–10]. However, it is still crucial to develop economic and efficient materials for improving optoelectronic properties of laser devices.

Graphene oxide (GO) has been widely employed in ultrafast optic, biosensing and heat storage [11,12]. GO exhibits high flexibility and processability. Moreover, it shows ultrafast recovery time and saturable absorption properties, which is similar to that of graphene [13–15]. Compared with graphene, GO may be easily dispersed in aqueous solution due to a large quantity of hydrophilic groups on its surfaces. GO is a cheap laser material for solid laser devices [16]. GO contains hydroxyl, carboxyl, carbonyl and epoxy groups. Effects of these oxygen-containing groups on ultrafast recovery time and saturable absorption properties of laser devices would be different, therefore, solid laser devices fabricated by GO with only one kind of oxygen-containing groups, for example, hydroxyl groups, could have good optoelectronic properties [17]. Compared with carboxyl, carbonyl and epoxy groups, hydroxyl groups have good chemical stability. Therefore, if GO were treated to develop a kind of new material with hydroxyl groups on its surfaces, the graphene oxide-like materials should be a potential optoelectronic materials.

Size of the nano materials affects the properties of laser devices fabricated by the materials. In general, laser devices fabricated by large size of graphene have excellent optoelectronic properties [17–19].

In this paper, a new type of graphene oxide-like with hydroxyl groups (GOLH) has been synthesized. It was characterized by fourier transform infrared (FT-IR) spectrum, X-ray diffraction (XRD), elemental analysis (EA), scanning electron microscopy (SEM), Raman spectra and dynamic light scattering (DLS). Its optoelectronic properties were investigated by a Q-switching laser. Experimental results suggested that GOLH would be employed as a saturable absorber. A Q-switched pulse laser with the GOLH materials exhibited stable signal intensity and narrow pulse duration, 0.8 μs. Therefore, the GOLH would be potential pulse laser materials.

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2. Experimental

2.1. Materials and methods

GO was prepared according to that in literature [20]. All other chemicals were purchased from Sigma-Aldrich. A digital light incubator was made from Jintan Kejie Equipment Company. FT-IR spectra were recorded on a Brucker Vector 22 spectrometer (USA), in which samples were embedded in KBr thin films. XRD were measured on a XRD-6100 shimadzu powder diffractometer (Japan). EA for carbon, hydrogen and nitrogen were recorded using a Vario ELE-III elemental analyzer (Germany). Raman spectra of samples were recorded on a Renishaw inVia plus Raman microscope. Surface morphologies of samples were taken by SEM performed on a HITACHI SU1510 SEM tester (Japan). Particle sizes of samples were confirmed by a ZETASIZER Nano zs90 DLS analysis.

2.2. Synthesis of GOLH

GO was prepared according to that in literature [20]. FT-IR spectrum of GO is in accordance with that in literature [20]. FT-IR (KBr): υ = 3424 (O–H), 1725 (C=O), 1618 (C=C), 1400 (O–H bending vibration), 1222 and 1056 (C–O–C) cm^{-1}.

GO (0.4 g) was added into water (800 mL) to give a suspension. The suspension was ultrasonicated (100 W) for 1 h. HCl (5 wt %) was added into the suspension to adjust pH value of suspension to 4. An aqueous solution of $MnSO_4$ (4 mL, 5.9 mM) and H_2O_2 (16 mL, 35 mM) were added into the suspension. The sample was irradiated with ultraviolet light (λ = 185 nm) at 25 °C for 2 days [20]. Then, solid was filtered and washed by water (3 × 200 mL) to give black crude product, degraded graphene oxide (DGO). The crude was dried at 200 °C under vacuum for 3 h to give black power, graphene oxide-like with hydroxyl groups (GOLH) (0.15 g).

2.3. Preparation of saturable absorber

GOLH (0.03 g) was added into water (50 mL) to give a suspension. The suspension was ultrasonicated for 1 h. The suspension (0.4 mL) was dropped on a quartz sheet (25 mm × 25 mm). The quartz sheet coated by GOLH was dried at 80 °C under vacuum for 6 h.

2.4. Experimental setup of GOLH based Q-switching laser

Experimental setup of the GOLH based Q-switching laser is shown in Fig. 1. Pump source was a fiber-coupled laser diode (LD) with a central wavelength of 808 nm. Diameter of fiber core with a numerical aperture of 0.22 was 400 μm. Pump light was focused on the Nd:YVO_4 crystal by using a focusing system with the beam compression ratio of 1: 1. A Nd:YVO_4 crystal cut along its a-axis was used as a laser gain medium. The dimensions of the crystal was 3 mm × 3 mm × 5 mm with the Nd^{3+} doping concentration of 0.5%. The Nd:YVO_4 crystal was wrapped with indium foil and mounted in a water-cooled copper block at 25 °C. Two mirrors were comprised in the resonant cavity: a plane-concave mirror (M1) and a flat mirror (M2). The input coupler mirror (M1) was anti-reflection (AR) coated at 808 nm and high reflection (HR) at around 1064 nm. The output coupler mirror (M2) has a transmission of 5% at the 1064 nm laser wavelength. The GOLH was used as the saturable absorber (SA). It was inserted next to M2. The temporal behaviors, for the Nd:YVO_4 fiber lasers, was recorded by using a fast response photodetector (Newport Model 818-BB-21) and a high speed oscilloscope (Agilent Technologies MSO7052B, bandwidth 500 MHz).

The nonlinear absorption property of GOLH sample was explored by a 170 fs laser operating with a centre wavelength of 800 nm at a repetition rate of 1 kHz (legend Elite-USP HE, Coherent Inc.) [25]. The GOLH SA film was prepared according to that in *Preparation of saturable absorber* part.

With a quartz sheet, the continuous wave (CW) Nd:YVO_4 laser was accomplished initially. We can obtained the 1064 nm TEM_{00} mode laser with power instability better than 5% by optimizing the parameters of the laser cavity. Then, substituting the quartz sheet with a GOLH SA and adjusting the position of the GOLH SA finely. The stable passively Q-switched operation was obtained and the total length of the cavity is 5.0 cm. Under the incident pump power of 3 W in this experiment, the Q-switching laser operation was appeared initially. The average output power increased practically linearly with the go up of incident pump power. At the same time, the wave profile pulse sequence was becoming more and more stable. However, with further increase of the incident pump power, it is greater than 6 W, the pulse sequence of the Q-switched laser became instability, appeared strong amplitude variation and the SA was damaged.

3. Results and discussion

3.1. Structure of GOLH

3.1.1. FT-IR spectrum

FT-IR spectra of GO, DGO and GOLH were shown in Fig. 2.

In FT-IR spectrum of GO, absorption peaks located at 3424, 1725, 1618, 1222 and 1056 cm^{-1} are attributed to O–H, C=O, C=C, C–O–C and C–O–C stretching vibration modes, respectively (Fig. 2). An absorption peak located at 1400 cm^{-1} is attributed to O-H bending vibration mode.

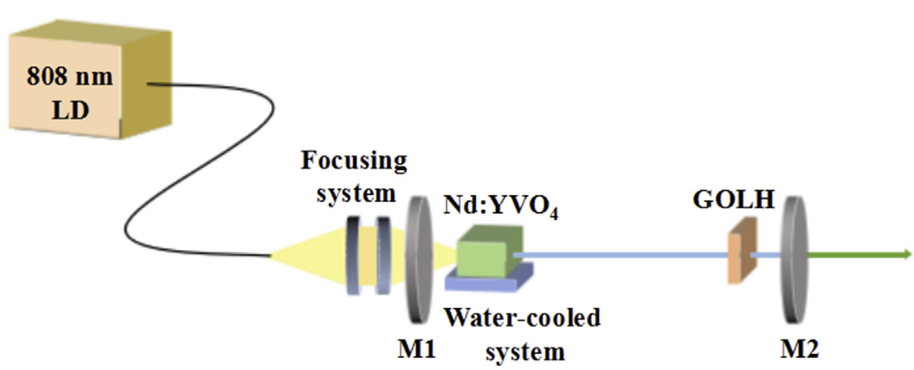

Fig. 1. Experimental setup of the GOLH based Q-switching laser.