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Improved field emission property of graphene by laser irradiation

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ABSTRACT

Graphene oxide (GO) can be reduced to graphene by either laser irradiation or thermal annealing. To improve the field emission (FE) property, a pulse CO_2 laser has been employed to irradiate GO films prepared by electrophoretic deposition (EPD). By varying the laser irradiation time, we were able to fabricate emitters with varied field enhancement factor. It has been found that the FE properties of laser irradiated films with optimized time 15 s were better than that of thermal annealed samples. The turn-on field (E_{to}) at 0.01 mA/cm^2 was reduced from 3.4 to 2.4 V/μm, and the threshold field (E_{th}) at 1 mA/cm^2 was reduced from 6.8 to 5.1 V/μm. Scanning electron microscopy (SEM) was taken to reveal the change of morphology after laser ablation, and it shows that the laser irradiation made great deal of graphene edges vertical to the substrate, which remarkably enhanced the FE properties. This kind of effective and convenience method made the graphene films as a potential field emitter for vacuum microelectronic devices.

1. Introduction

With outstanding properties in many fields and promising applications [1–4], graphene has drawn more and more attention in recent years. Due to unique two-dimensional (2D) structure, it has been widely studied in nano-electronic devices [5–8], such as transparent electrodes and electrochemical capacitors. The excellent electrical conductivity and high aspect ratio (the ratio of lateral size to thickness) also made it a potential field emission (FE) material [9,10]. Graphene grown through chemical vapor deposition (CVD) had disadvantages when it came to low-cost production. But chemical oxidation was proved to be inexpensive and mass producible, which showed the great expectation for applications [10,11]. Moreover, graphene oxide (GO) prepared by chemical oxidation could be easily dispersed in solution and naturally fit for electrophoretic deposition (EPD).

EPD was a commonly industrial deposition technique for fabricating thin films. And it has also been widely used to fabricate nano-materials, such as carbon nanotubes (CNTs) [12] and graphene [10,11,13] based FE cathodes. Therefore, GO films were prepared by EPD in this study.

Previous studies reported that the FE properties of CNTs [14,15] and other materials [16] would be greatly enhanced and the surface morphology changed after laser treatment. With similar structure, graphene may also have the opportunity to improve the FE properties by laser irradiation. Therefore, we employed CO_2 laser to irradiate GO films. For comparison, other films without laser treatment were annealed under argon atmosphere at different temperatures. Then we compared the FE of GO films after laser irradiation or thermal annealing.

One of the most serious problems of the graphene cathodes prepared by existing deposition methods was the relative small enhancement factor (β), because many graphene sheets were horizontally on the substrate [17]. To overcome such drawback, laser irradiation was introduced to change the surface morphology, and more graphene edges would turn vertical to the substrate and increase the enhancement factor (β).

2. Experimental

2.1. Preparation of GO suspension

GO powder we used in this study was prepared by modified Hummers' method [18], as we reported elsewhere [11,19,20]. As an initial step, 100 mg GO powder with half weight ratio of $Mg(NO_3)_2{\cdot}6H_2O$ were put into 100 mL isopropyl alcohol and then

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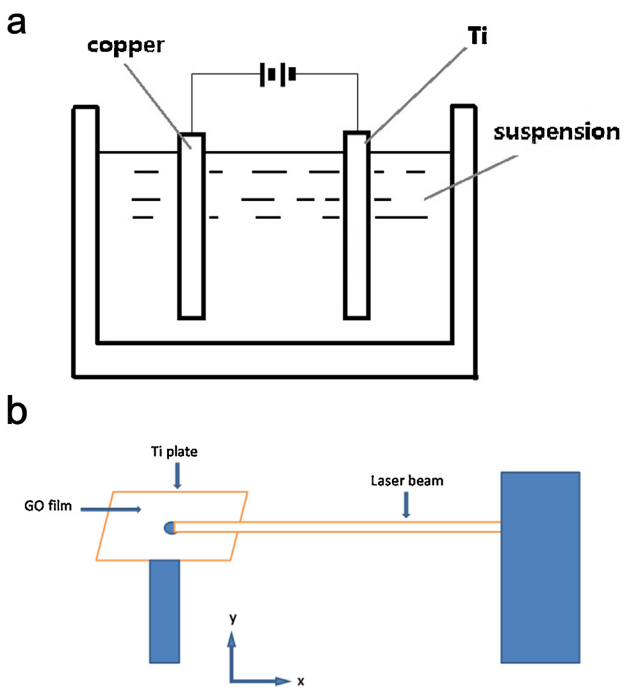

Fig. 1. (a) Scheme of the EPD process. (b) Scheme of the experimental setup for laser irradiation.

ultrasonication at 120 W for 1 h. The Mg^{2+} was absorbed on GO surface, and made GO stable dispersion in the suspension.

2.2. Electrophoretic deposition process

Fig. 1(a) shows a schematic diagram of EPD. A titanium (Ti) plate was used as substrate, and a copper plate as positive electrode. The size of Ti plate was 7.5 cm × 2.5 cm ($L \times W$), and GO film could cover all over the Ti plate. For the convenience of laser treatment, we make a mask of polyethylene with the same size of Ti plate and we made a hole with the diameter of 4 mm on the mask. So after EDP GO was only on the position of the hole. The distance of the two electrodes was 10 mm. Constant voltage of 150 V was applied between the two electrodes for 4 min. After deposition, these films were dried in air.

2.3. Laser treatment and thermal annealing

Then a pulse CO_2 laser with wavelength at 10.6 μm was used to irradiate GO films for 2, 5, 10, 15, and 20 s in air respectively. The irradiation laser was parallel light and the distance between the laser and sample was about 1 meter. The scheme of the laser treatment setup is shown in Fig. 1(b). Different areas can be treated by translating the sample with horizontal and vertical dimensions. The power of laser was 20 W. After irradiation, it can be found that the color changed from red to black. Other samples prepared in the same deposition condition without laser treatment were annealed in argon atmosphere at 400, 500, 600 and 700 °C for 40 min, respectively.

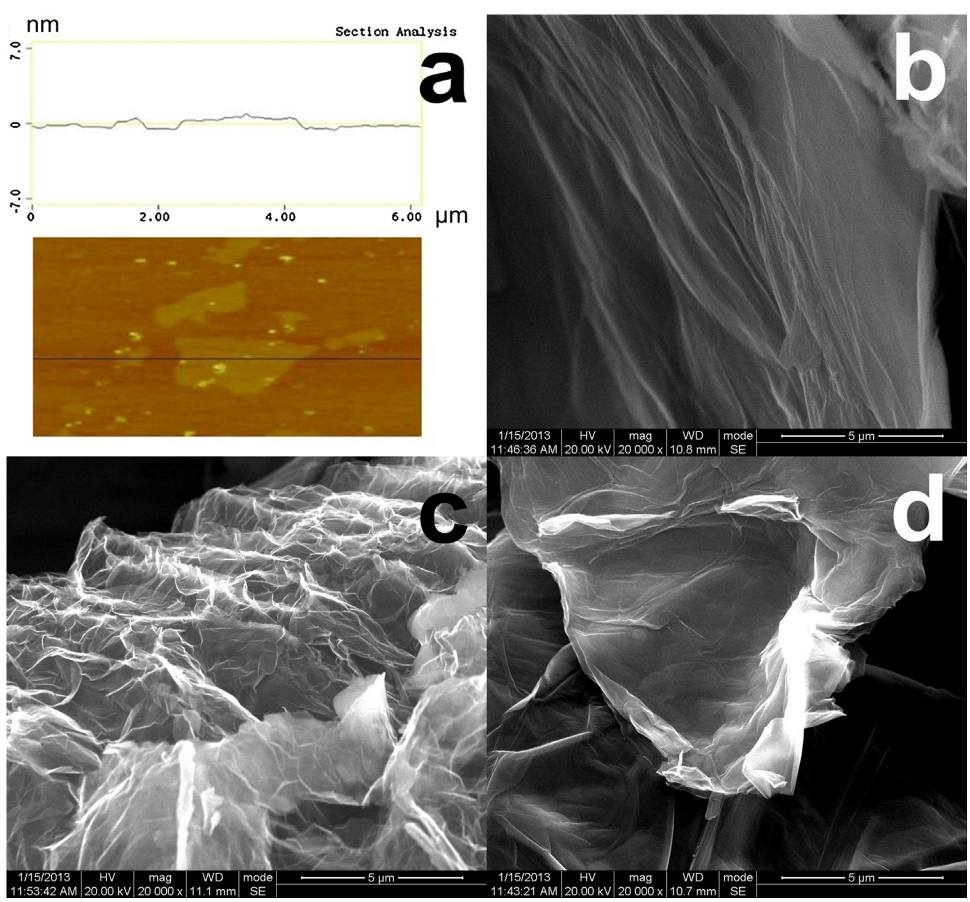

Fig. 2. (a) AFM image of the pristine GO sheets. (b) SEM image of the pristine GO film after EDP. (c) SEM image of the film after laser irradiation for 15 s. (d) SEM image of the film annealed at 600 °C.