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Mask-free and programmable patterning of graphene by ultrafast laser direct writing

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ABSTRACT

Reported here is a mask-free and programmable patterning of graphene by using femtosecond laser direct writing on graphene oxide (GO) films. Take advantage of the ultrahigh instantaneous intensity of the femtosecond laser pulse, and especially its nonlinear interactions with materials, the GO could be efficiently reduced under atmospheric condition at room temperature. Moreover, the designability of femtosecond laser direct writing (FsLDW) technique allow making graphene micropatterns arbitrarily according to the preprogrammed structures, which provides the feasibility for rational design, flexible fabrication and integration of graphene-based micro-devices. Raman spectra show that the reduced and patterned region is very homogeneous, which is confirmed by the almost consistent I_D/I_G ratio. The novel graphene patterning technique would provide a technical support for the development of graphene-based micro-devices for future electronics.

1. Introduction

Recent years have witnessed a rapidly increased research interest in graphene and its related materials. Ever since the first discovery of this unique one-atom-thick carbon crystal, graphene has revealed a cornucopia of both fundamental research and potential applications due to its exceptional properties, such as ultrahigh electron mobilities [1], high thermal conductivity [2], mechanical strength [3], flexibility [4], excellent stability [5] and optical transparency [6]. All of these unique properties make graphene a promising candidate material for nanoscale electronic devices, such as electrodes [7,8], sensors [9] and transistors [10]. Currently, graphene could be readily prepared by chemical vapor deposition (CVD) with Cu [11] or Ni [12] substrate as catalysts. However, the application of CVD graphene suffers from complex substrates transferring procedure, significantly limiting its practical use in electronic devices. Alternatively, graphene oxide (GO) prepared from chemical oxidation of raw graphite shows distinct advantages in mass production and solution processability [13–18]. Generally, GO sheets consist of a graphitic carbon network bearing various types of oxygen-containing defects that render the sheets solubility in water, which allows the tractable processing and dispersion of isolated sheets or multilayer films from aqueous solutions. However, due to the high oxygen level in GO, there exist a lot of defects which seriously affect its electrical properties. And therefore, removal of oxygen containing groups of GO becomes necessary for its further application in electronics [17,19–20].

On the other hand, besides the reduction procedure, rational design and patterning of graphene is of considerable importance for the fabrication and integration of graphene-based devices [21–23]. However, the currently available patterning techniques including classical lithography [24], O_2 plasma etching [25], and flash reduction [26] usually need protected layer or a shadow mask to define the desired micropatterns. In the mask-defined pattering, different micropatterns usually need different masks. Moreover, the substrates should be very smooth and the tight contact between the graphene/RGO (reduced graphene oxide) and the mask layer would inevitably cause breakage or contamination of the graphene films. Therefore, mask-free methods that could be used for making graphene micropatterns are highly desired. In addition, novel patterning approaches such as reduction and patterning of GO by using a heated AFM-tip [27], and a combination of modulating the solution wettability of the substrates and spin-coating process [28] are also adopted for making graphene micropatterns. However, these methods depend on special instrument or precise treatment of substrate and suffer from low efficiency. Recently, photoreduction of GO by using various laser shows the feasibility for making graphene micropatterns in a non-contact manner, revealing great potential for fabrication and integration of

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graphene-based micro-devices [28–33]. However, in order to achieve a relative high conductivity, the laser reduction should be carried out with the protection of inert gases, which not only limits the patterning area, but also brings considerable complexity for the device fabrication, and especially integration with other devices. Therefore, a mask-free and designable patterning of GO under atmospheric condition at room temperature is of critical importance to the development of graphene-based micro-devices, but obviously, it remains a technical challenge.

It is remarkable that, as an ultrafast laser, femtosecond laser pulse has been widely used for designable fabrication of three-dimensional (3D) microstructures with high spatial resolution due to its ultrashort pulse, ultrahigh instantaneous intensity and nonlinear interactions with various materials [34–40]. In this work, ultrafast laser pulse was adopted to fabricate reduced graphene micropatterns by direct writing on GO films according to the predetermined computer programs. In the case of femtosencond laser process, no mask is needed for the patterning, so hereafter, we called this method as "mask-free" patterning of graphene. Experimental results show that the reduced and patterned GO film is conductive, and exposure duration could be used to control its electrical conductivity. In addition, the laser reduction is also a chemical-free and "green" process, which means no chemical reagent is used during the reduction of GO. Thus, the mask-free, chemical-free and programmable patterning of GO films holds great promise for fabrication and integration of graphene-based micro-devices for future electronics.

2. Experimental

2.1. Preparation of GO

Graphene oxide was synthesized using a modified Hummer's method [41] from purified natural graphite. In typical procedure, 2 g of natural graphite flake, 2 g of $NaNO_3$, and 100 mL of concentrated H_2SO_4 (98%) were mixed at 0 °C under stirring. Then, 15 g of $KMnO_4$ was gradually added into the above mixture under stirring at 0 °C for 90 min, and at 35 °C for 2 h, respectively. After addition of 300 mL of distilled water slowly to the resulting solution, 10 mL of H_2O_2 (30%) was dropped into the mixture to reduce the residual $KMnO_4$, and finally graphite oxide suspension was obtained. The GO sample was collected by high-speed centrifugation and repeatedly washed with distilled water for several times until the pH reach 7. For the preparation of GO suspension, GO was diluted with water at a concentration of 3 mg/mL with the aid of ultrasound. The GO films were prepared by spin-coating GO solution on glass substrate at 1000 rpm for 30 s, dried at 60 °C for 1 h. The thickness of the GO films is about 60 nm. Gold electrodes were evaporated on the GO film under vacuum through a pattern mask. The sample was used for further processing by femtosecond laser.

2.2. Patterning of GO

For the patterning and reduction of GO film, a femtosecond laser pulse with 800 nm central wavelength, 120 fs pulse width, 80 MHz repetition rate was focused by a × 100 objective len with a high numerical aperture (NA = 1.4) into the GO film. 500–900 μs exposure duration of each voxel and 100 nm scanning step length were adopted for different samples. Then the femtosecond laser directly wrote on the GO film according to preprogrammed patterns. The as fabricated micropattern was designed by Photoshop.

2.3. Characterization

The femtosecond laser was generated by Tsunami, Spectra-Physics lasers (model: 3960-X1BB s/n 2617; ccd: AMSTAR, B/W; video ccd: CAMERA). Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer. The 514.5 nm radiation from a 20 mW air-cooled argon-ion laser was used as the exciting source. Atomic force micrographs (AFM) were obtained to use a NanoWizard II BioAFM (JPK Instrument AG, Berlin, Germany) in the tapping mode. SEM experiments were performed on a JEOL JSM-7500F scanning electron microcircuits, which were measured from a Keithley SCS 4200 semiconductor characterization system. Optical micrographs were obtained from a Motic BA400 microscope and the Charge Coupled Device (CCD) of the laser. X-ray photoelectron spectroscopy (XPS) was performed by using an ESCALAB 250 spectrometer. Spectra were baseline corrected by using the instrument software.

3. Results and discussion

Fig. 1 shows the schematic illustration of the femtosecond laser direct writing system that is used for the mask-free and programmable patterning of GO. A femtosecond laser with 80 MHz repetition rate, 120 fs pulse width and 800 nm central wavelength was focused by a 100 × oil immersion objective len to direct write various predesigned micropatterns on GO films. The laser scanning path was precisely controlled by computer according to the preprogrammed structures. During the fabrication, the entire process including the focusing of laser beam and the positioning of sites to be addressed was monitored by the Charge Coupled Device (CCD) set showing the feasibility for flexible fabrication of desired devices and even post integration.

In the ultrafast laser patterning of GO film, the laser intensity plays an important role for the formation of well defined micropatterns. Fig. 2 shows the GO micropattern fabricated under different laser powers. When the laser output power is too low (Fig 2(a)), the patterning is not very clear, because the GO pattern was only reduced slightly. On the contrary, when the laser power is too high, some of the laser scanned region were ablated, leaving a broken micropattern. Only if an appropriate laser power was used for the patterning, well defined micropatterns could be achieved. As shown in Fig. 2(c), the pattern is very uniform and continuous. In our work, the laser output power between 3 mW and 8 mW was considered as a suitable range for the patterning of GO. In addition to the optical microscopic image, the patterned GO film was also characterized by SEM. As shown in Fig. 2(d), the laser scanned region could also be distinguished from the pristine GO. Compared with the GO film which contains typical wrinkles, the patterned region was very smooth. It is worth pointing out that our mask-free and programmable patterning of GO is not limited to simple linear microstructures. In fact, any desired micropatterns could be

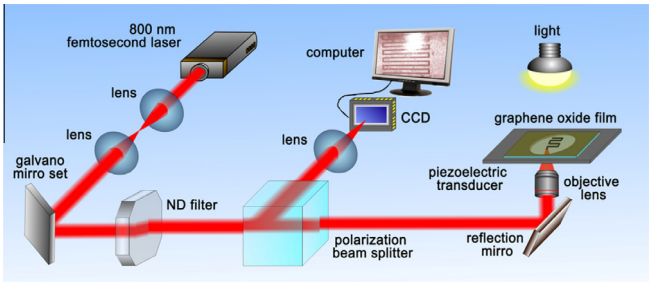

Fig. 1. Schematic illustration of the femtosecond laser direct writing system for mask-free and programmable patterning of graphene.