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Optical and magnetic properties of porous graphene films produced by electrospraying

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ABSTRACT

Graphene films have been produced by electrospraying on SiO_2-coated silicon substrate and subsequent heat treatment, offering a simple and typical method to produce porous graphene films and exhibiting a good adhesion to silicon substrate. The microstructures of as-prepared graphene films were characterized by field emission scanning electron microscopy, transmission electron microscopy, selected area electron diffraction and atomic force microscopy. X-ray photoelectron spectroscopy, infrared spectroscopy and Raman spectroscopy further confirmed the formation of porous graphene films. Moreover, the reflection spectrum of as-prepared graphene films was studied by ultraviolet–visible spectroscopy, revealing that light absorption played dominant roles at 375 and 635 nm, respectively. Finally, the resistance and magnetoresistance were measured, and some preliminary theoretical explanations were proposed.

1. Introduction

Graphene, a monolayer of sp^2-bonded carbon atoms with a two-dimensional (2D) structure and one-atom thickness [1], has been attracting great interests because of its distinctive band structure, excellent physical properties such as electronic, mechanical, optical, thermal properties [2–7]. Therefore, graphene exhibits a great promise for potential applications, such as field-effect transistors [8], light emitting diodes [9], and gas sensors [10,11]. Nowadays, much attention has been focused on the production of graphene films showing remarkable electron-field-emission characteristics [12], considerable opto-electrical properties [13,14], high electrical conductivity and optical transmittance [15].

Currently, a wide range of physical and chemical routes can be employed to produce graphene films, mostly using graphene dispersion as raw materials. Briefly, several methods developed so far in previous reports can be recommended as follows: spray-coating deposition [16], filter deposition [17], spin-casting deposition [18]. Moreover, method of chemical vapor deposition [1,13] is also playing a certain role in producing graphene films and displaying admirable advantages. Nevertheless, apart from its merits, problems of expensive device, high cost in raw materials, poor productivity and complicated process are existing in producing graphene films [1,19].

In this paper, we described a simple and typical method to produce porous graphene films by electrospraying on SiO_2-coated silicon substrate and subsequent heat treatment. Advantages of simplicity in preparation, low cost in raw materials and easily controlled make it possible for mass production in practical application. Our work started with preparation of graphene dispersion by using liquid phase exfoliation under sonication, and then the disordered, porous graphene films were produced by electrospraying. Additionally, the optical and magnetic properties of porous graphene films were analyzed by a series of characterizations and measurements.

2. Experimental section

2.1. Preparation of precursor solution

The method to produce graphene films includes three parts. One is the preparation of precursor solution [20] as follows:

(a) 2.5 g of graphite powder (99.85 wt.%) and 100 ml of N-methylpyrrolidone (NMP) were both added into a beaker, and then sealed up the beaker with multilayer preservative film.
(b) The above mixture after fully mixing was under sonication for 78 h in a low-power ultrasonic bath (~100 W, 40 kHz), and then the dispersion was left to stand overnight to allow graphite aggregates to form.
(c) The graphite aggregates was removed by centrifugation at 8000 rpm for 30 min to obtain a homogeneous, stable solution of graphene/NMP [21] with a concentration as high as 0.6 mg/ml.

2.2. Silicon wafer cleaning

The silicon wafer (coated with a 300-nm-thick SiO_2 layer) was rinsed with ethyl acetate and soaked in acetone, which was then under sonication with ethanol and distilled water successively. Finally,

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put it under an infrared lamp for several minutes to acquire a clean and dry silicon wafer.

2.3. Fabrication of porous graphene films

20 ml of graphene/NMP dispersion that we prepared above was loaded into a plastic syringe and the feeding rate was 0.2 ml/h, and the silicon substrate temperature was controlled at 200 °C to accelerate the evaporation of the residual NMP. Meanwhile, a high voltage of 8.6 kV (PS/FC12P10.0-22, Gamma High Voltage Research Inc.) was applied between the nozzle and the laboratory stirrer/hot plate (PC-220, USA) and the distance between the tip of the needle and the collector was about 7 cm [22]. Finally, after the electrospraying, the as-produced films were placed in an oven for 10 h at 200 °C to achieve porous graphene films we need.

2.4. Characterization

Structures of porous graphene films were studied by field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan) operated at 10 kV, transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) employed at 200 kV and atomic force microscopy (AFM, Nanonavi E-Sweep, SII, Japan) worked in contact mode. X-ray photoelectron spectroscopy (XPS) analysis was performed using Escalab 250 apparatus operated at 150 W and equipped with a monochromatic Al Kα radiation source ($h\nu = 1486.6$ eV), and consisted of a survey scan from 0 to 1350 eV. 20 eV pass energy and 0.05 eV energy increment were used in high-resolution spectra acquisition and charge correction was made with respect to adventitious carbon to which was assigned a binding energy of 285.0 eV. Data were interpreted using VG Avantage 4.53 software package. The infrared spectrum was recorded in the spectral range from 400 to 4000 cm^{-1} on a Perkin Elmer 1725X Fourier transform infrared spectrometer (FTIR) with 2 cm^{-1} resolution in the air at room temperature. Raman spectroscopy was carried out using DXR microscope (Thermo Fisher, USA) and the excitation source was a 532 nm line of an Nd^{3+}:YAG laser with power at the sample surface of 10 mW.

Optical absorption property was characterized by ultraviolet–visible (UV–vis) spectroscopy (UV-3101 PC, Shimadzu, Japan). The magnetoresistance (MR) was investigated using a standard four-probe technique in a Physical Property Measurement System (PPMS, PPMS-9T, Quantum Design, USA) in the temperature range from 6 to 50 K and magnetic field from 0 to 6.0×10^6 A/m on rectangle samples (10×5 mm^2). The resistance vs. temperature was also done in the temperature range of 50–300 K. The contact pads were fabricated by conductive silver paste with Pt electrodes.

3. Results and discussion

3.1. TEM, AFM and FESEM

Fig. 1 shows the TEM images of the NMP/graphene dispersion. The randomly stacked and folded graphene multilayer, few monolayers are emerging in Fig. 1(a) and (b), respectively. As presented in Fig. 1(b), the margin of few-layered graphene is clear and the corresponding selected area electron diffraction (SAED) pattern on the inset of Fig. 1(b) further demonstrates the preparation of few-layered graphene [23]. AFM is also carried out to intuitively estimate the thickness of the graphene we obtained (Fig. 2). The height of the selected two points is 1.17 nm on mica substrate, noting that this graphene has approximately 3 layers.

FESEM is used to reveal the morphology of porous graphene films, as shown in Figs. 3 and 4 with different magnifications after heat treatment. Intriguingly, morphologies of disordered arrays, highly porous structure and favorable continuity can be clearly observed in Fig. 3(a, b). In addition, no graphite particles are found except the graphene flakes in graphene films (Fig. 3(c, d)), demonstrating a homogeneous, stable dispersion of graphene/NMP which has been prepared.

In order to have a further study of porous graphene films, the FESEM micrographs of cross section of the as-prepared samples are presented in Fig. 4. The thickness varies from 30 to 50 μm, shown in Fig. 4(a, b). Moreover, the films are found to adhere strongly to the substrate, although there is ever a weak force applied on graphene films to attain the cross section.

Obviously, morphologies of disordered arrays and highly porous structure found in Fig. 4(a, b, c) can exhibit a higher specific surface area and promising electrical performance showing significant potential applications in gas sensor, lithium battery and catalyst. Furthermore, it is worth noticing that most of the graphene flakes adhere to the substrate are upright standing (Fig. 4(d)), opening a door to the fabrication of high-performance graphene-based electronic and magnetic devices [24].

3.2. XPS, FTIR and Raman

XPS survey results of the porous graphene films are shown in Fig. 5. The peak at 532.5 eV (Fig. 5(a)) shows a high oxygen signal in the as-prepared films. The high-resolution XPS carbon 1s (C 1s) spectrum (Fig. 5(b)) associated with graphitic carbon (C–C) is dominated by a feature around 284.6 eV. We also observe other additional peaks with four components through fitting procedures,

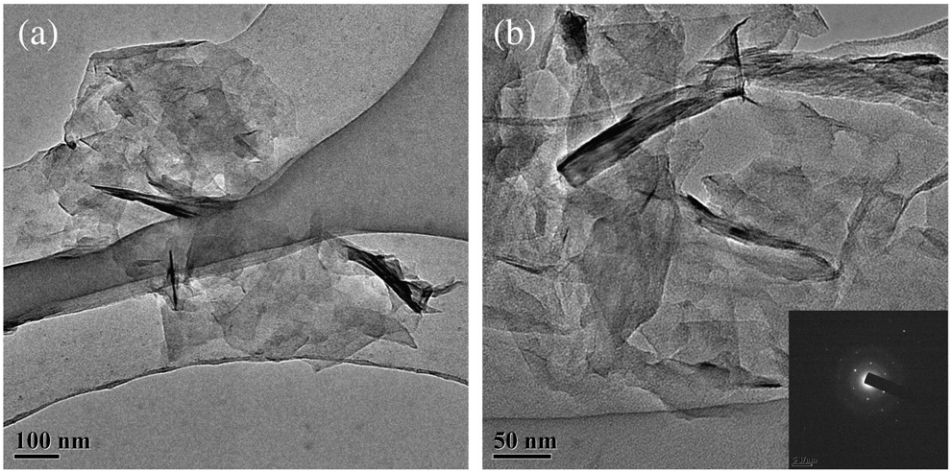

Fig. 1. TEM images of the NMP/graphene dispersion. Inset of (b) is the SAED pattern of graphene layers.