



Study of electrical conductivity and photoelectric response of liquid phase exfoliated graphene thin film prepared via spray pyrolysis route

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Abstract

Facile process for the fabrication of multi-layer graphene thin film (MLGF) is reported here. Multi-layer graphene dispersion prepared by liquid-phase exfoliation of graphite was sprayed on a glass substrate by spray pyrolysis method. The structural, optical and electrical properties of the deposited MLGF are investigated. The sheets of graphene are deposited uniformly on the substrate and distribution of small graphene sheets with size of 300–500 nm can be observed in SEM image. AFM and micro-Raman results ensured that the spray-coated graphene thin film is composed of multi-layer graphene sheets. Spray coated graphene thin film showed significant optical transparency of 57% in the visible region (400–550 nm). MLGF possessed the electrical conductivity in the order of 744 S/m with surface resistivity of 3.54 k Ω /sq. The prepared liquid-phase exfoliated graphene thin film showed superior photoelectric response. The results of this study provided a framework for fabricating an optimized MLGF using a spray pyrolysis route for optoelectronics devices.

Keywords Graphene thin film · Liquid phase exfoliation · Spray pyrolysis · Raman intensity mapping · Electrical conductivity · Photoconductive response

1 Introduction

More than a decade, graphene is a fascinating material used in a wide range of applications such as gas sensor, supercapacitors, Li-ion battery, solar cells, flexible electronic devices and photocatalysis, because of its outstanding and attractive properties [1–3]. Different physical methods namely mechanical exfoliation, chemical vapor deposition (CVD), epitaxial growth on silicon carbide, arc discharge method, and substrate-free gas-phase synthesis were used for the preparation of high-quality graphene in large scale [4]. But difficulties in the creation of high-temperature control over cooling rate, pressure and requirement of high-quality substrate materials are standup barriers to the above mentioned methods for the production of graphene in large scale.

Later days, large scale synthesis of graphene sheets were achieved by a chemical method called Hummer's method/

modified Hummer's method to produce reduced graphene oxide (rGO) sheets as a final product [5, 6]. Liquid-phase exfoliation (ultrasonication of pristine graphite powder in suitable organic solvents) is an another simple and low-cost solution process method compared to other methods for the production of a high-quality single layer to few-layer graphene sheets with significant yield and good electrical conductivity [7, 8].

However, the graphene sheets synthesized by the solution process can be effectively used in various devices only after converting them in the form of thin films. The application of the reduced graphene oxide prepared by Hummer's method was promoted by transferring them as thin film by spray pyrolysis method [9, 10]. Though the production of reduced graphene oxide by Hummer's method involved various tedious oxidation and reduction processes and the functional materials present in the reduced graphene oxide may have an effect on its electrical and optical properties. Some of the researchers have tried to fabricate the thin film of liquid phase exfoliated graphene by vacuum filtration method using membrane of alumina [7], PTFE [11], nylon [12] and MCE [13], which are having the disadvantages of high cost and less possibility of transferring the film to other substrate for application purposes.

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There are few reports on the thin film of liquid-phase exfoliated graphene via spray pyrolysis, dip coating and dielectrophoresis [14–16]. Among them, spray pyrolysis technique is the simplest method for the fabrication of thin films since it is cost-effective, involves simple technical apparatus and it is suitable for large-scale production of uniform and high-quality thin films with desirable crystallinity [17]. This method is more reliable for the fabrication of thin films with high electrical and optical parameters as it does not require high vacuum or/and operating temperature [18]. However, the reports on the preparation of graphene thin film by spray pyrolysis of liquid-phase exfoliated graphene and the detailed investigation on their electrical properties are hard to find. Sales et al. [16] have reported the current–voltage characteristics of the spray-coated thin film of graphene exfoliated in ethanol-deionized water solution. The electrical properties of the liquid phase exfoliated multi-layer graphene thin film prepared by dip-coating method is reported by Machunoa [14].

In the present work, we have prepared the graphene dispersion by liquid-phase exfoliation of graphite in *N*–*N'* dimethylformamide and transferred the graphene dispersion as a thin film by spray pyrolysis technique. This report includes the investigation of structural, morphological, electrical as well as photo conducting properties of the fabricated graphene thin film. The main focus of our work is to provide an insight to the electrical and photo conducting properties of the liquid phase exfoliated graphene thin film to provide a platform for the promotion of the liquid phase exfoliated graphene to the application level using facile and cost-effective method.

2 Experimental procedure

2.1 Preparation of graphene dispersion

Graphite powder and *N*–*N'* dimethylformamide (DMF) were used for the preparation of graphene dispersion by liquid-phase exfoliation. 100 mg of graphite powder was mixed with 50 ml of DMF and sonicated for 8 h using an ultrasonic bath sonicator. After ultrasonication, the graphene dispersion was centrifuged with 3000 rpm for 30 min to separate the thin graphene flakes. The 25 ml of supernatant dispersion was collected for the preparation of the thin film.

2.2 Preparation of graphene thin film

The exfoliated graphene dispersion was deposited on a glass substrate ($2.5 \times 2.5 \times 0.15 \text{ cm}^3$) by chemical spray pyrolysis technique. Before the deposition of the graphene precursor, the substrate was cleaned by 15 min of successive ultrasonication in double distilled water, acetone, and ethanol baths.

The well-cleaned substrate was then kept on the hotplate of the spray pyrolysis unit at 120 °C. The nozzle to substrate distance was carefully maintained as 14 cm. Nearly 50 ml of graphene dispersion obtained by the above-mentioned procedure was sprayed onto the preheated glass substrate at a spray rate of 1 ml/min. The compressed air was used as a carrier gas. The thickness of the deposited thin film is $380 \pm 10 \text{ nm}$. Finally, the thin film was dried at 250 °C for 3 h.

2.3 Characterization techniques

Powder XRD pattern of the graphene thin film was recorded using PANalytical Empyrean with Cu- K_{α} radiation. The thickness of the prepared graphene film was measured using Dektak 3030 Stylus Profilometer. The UV–Vis transmittance spectrum was recorded using SHIMADZU UV-2450 spectrophotometer and the surface morphology of the sample was analyzed using SEM (FESEM; Nova NanoSEM 230), TEM (HRTEM; JEOL, JEM 2100), and AFM (A100 SGS, APE Research). Room temperature micro-Raman spectra were recorded using HORIBA Jobin–Yvon LabRAM HR 800 using a He–Ne laser of wavelength 632.8 nm as an excitation source. Raman spectra of nearly 100 points were collected and the Raman intensity map was constructed for the area of $(22 \times 22) \mu\text{m}^2$. The electrical conductivity at room temperature was measured using the Ecopia HMS-3000 Hall measurement setup in Vander Pauw configuration. The photoconductivity measurement was carried out in a vacuum chamber using a Hind High Vacuum cryostat facility instrument at ambient temperature.

3 Results and discussion

The measured XRD pattern of the graphene thin film and graphite powder are shown in Fig. 1. The X-ray diffraction peak is obtained at 26.53° for graphene thin film and 26.67° for graphite powder. Obtained diffraction peaks of both graphene thin film and graphite powder are well matched with the JCPDS no [75-1621] and other reports [19, 20]. The corresponding inter-planar distance of graphene thin film and graphite powder are 3.36 and 3.34 Å, respectively. The observed increase in inter-planar distance of graphene thin film from that of graphite powder indicates the successful exfoliation of graphene sheets from graphite powder. Sharp diffraction peak of graphene shows that the high-quality graphene crystalline thin films are successfully deposited using spray pyrolysis technique.

Figure 2a, b show the SEM images of the graphene thin film captured at different places on the film surface. Distribution of smaller graphene sheets with a length of 300–600 nm can be seen on the surface of the thin film (Fig. 2a). The

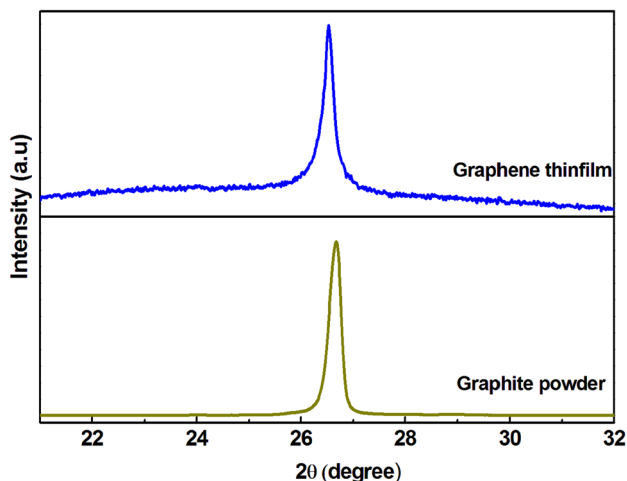


Fig. 1 XRD pattern of graphite powder and graphene thin film

surface of the thin film also contains larger size graphene sheets stacked on one another with lateral size varies from 1.2 to 3.2 μm (Fig. 2b). TEM image (Fig. 3a) clearly shows the stacked graphene sheets with a lateral size of ~ 350 nm and a width of 225 nm. In Fig. 3b, thin graphene sheets with a lateral size of 500 nm can be observed.

Further, the surface morphology of the graphene thin film was analyzed using the AFM and its image is shown in Fig. 4. The variation in the thickness of the graphene sheets can be observed through the brightness in the AFM image which also supports the existence of smaller graphene sheets on the surface of the uniformly coated graphene thin film as

observed in SEM image. The approximate lateral dimension of the graphene sheet marked in the AFM image is ~ 1.1 μm and the estimated average thickness varies from ~ 11 to 20 nm. This thickness value approximately corresponds to the multilayer graphene with the number of layers varies from 22 to 40 and is comparable with the graphene sheet thickness reported in dip-coated graphene thin film [14].

The transmittance spectrum of the graphene thin film is shown in Fig. 5a. It shows a broad transmittance band from 600 to 350 nm and shows around 57% of transparency in the region 400–550 nm. However, the obtained transmittance is higher compared to that of dip-coated [14] and plasma-treated spray-coated graphene thin films [16] and lesser than the transmission of the single-layer graphene sheet ($T \sim 98\%$) [21]. Hence, it can be inferred that graphene thin film prepared in the present case shows better optical transmission in the middle of the visible spectrum than the previous reports. The reduction of transmittance and increase in absorption than the single layer may be due to the multi-layer nature of the graphene and the higher thickness of the film [22].

In Fig. 5b the observed Raman bands of graphene film at 1319 cm^{-1} (D band), 1564 cm^{-1} (G band) and 2647 cm^{-1} (2D band) are characteristic Raman bands of graphene [23]. The shifting of band positions to the low wavenumber compare to that of graphite and changing of the broad asymmetric 2D band of graphite into a sharp symmetric band in graphene film revealed that the method used for the preparation of thin film from the exfoliated graphene dispersion does not lead to the re-aggregation of graphene into graphite. The increase in the intensity of D band from that of graphite

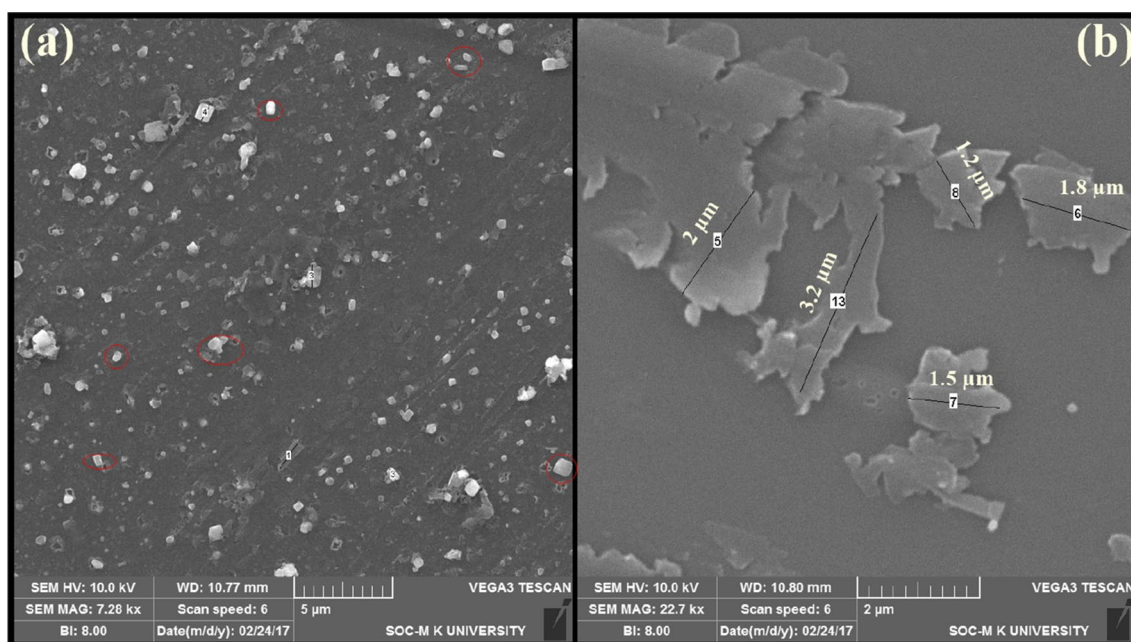


Fig. 2 (a, b) SEM images of the graphene thin film

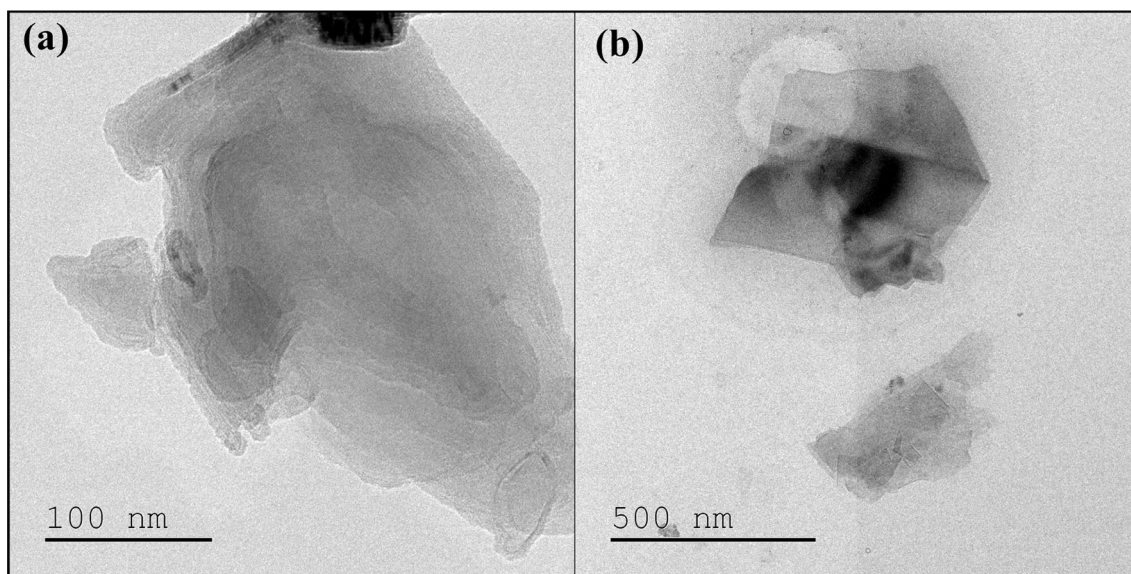


Fig. 3 (a, b) TEM image of the graphene thin film with different magnification

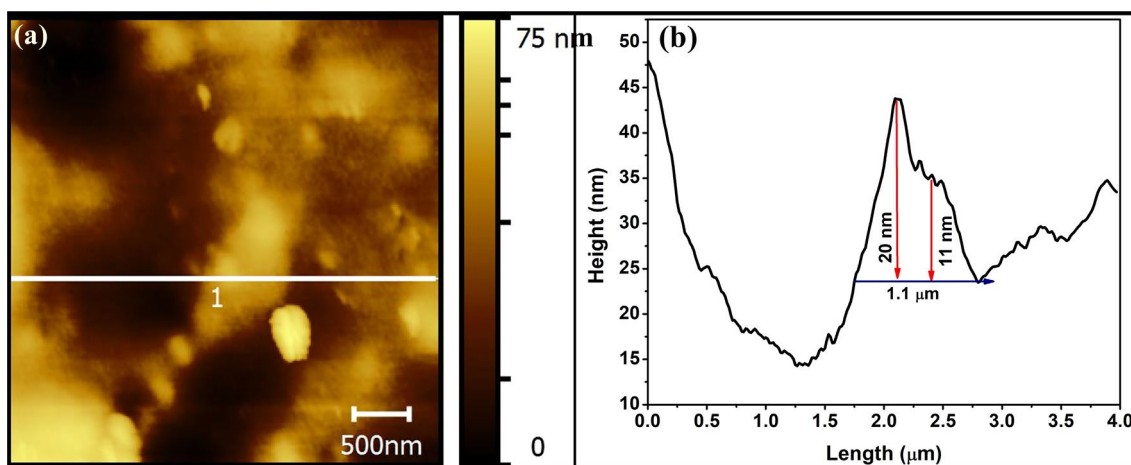


Fig. 4 (a) AFM image of the graphene thin film (b) corresponding height profile of the marked line in the image

is due to the edge defects created during the exfoliation process [12].

Micro-Raman intensity mapping was performed for a selected area of $20 \times 20 \mu\text{m}$ to study the average structural quality and number of graphene layers. Figure 6a–c shows the integrated intensity image of D, G and 2D bands constructed by scanning the selected area and collecting the intensity data at each spot. The high intensity bright and low-intensity dark regions in D, G, and 2D band indicate the uniformity of the number of layers and defects of graphene over the coated area of the thin film. The bright regions are attributed to the D, G and 2D bands with higher intensity whereas the dark regions are related to their lower intensity. The I_D/I_G and I_G/I_{2D} were calculated

from the intensity values of each band collected at 100 different points and their histogram are shown in Fig. 6d, e. The I_D/I_G ratio gives the evidence of the structural defect in the graphene whereas I_G/I_{2D} ratio gives the information about the number of layers of graphene flakes. From the histogram of I_D/I_G and I_G/I_{2D} obtained from the intensity mapping data (Fig. 6d, e), it can be concluded that I_D/I_G ratio related to the structural defects in the graphene varies from 0.2 to 0.6 and I_G/I_{2D} ratio, indicating the number of layers in the graphene sheets, varies from 2 to 3.5. As per the relation reported in Ref. [16], the calculated number of graphene layers (n) using I_G/I_{2D} ratio varies from 18 to 33. This result is well agreed with the thickness value measured through AFM image. These results inferred that

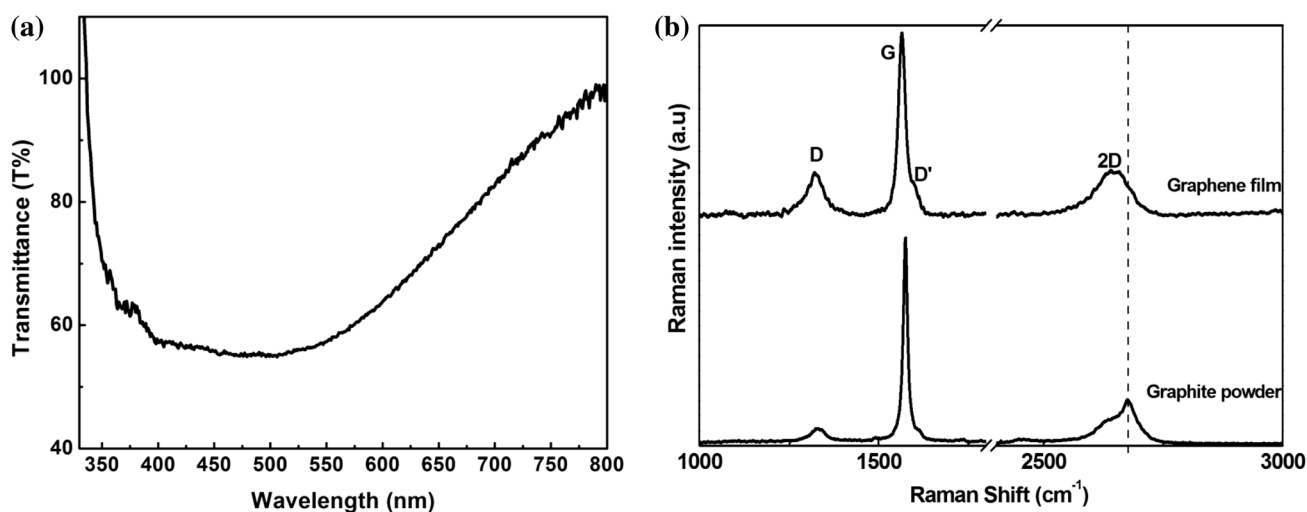


Fig. 5 (a) Optical transmittance spectrum of graphene thin film (b) micro-Raman spectrum of graphite powder and graphene thin film

the spray-coated graphene are multi-layer graphene (MLG) sheets with very fewer edge defects [24].

The electrical conductivity of the graphene thin film is ~ 744 S/m and the surface resistivity is ~ 3.54 k Ω /sq. This value of electrical conductivity is relatively higher than that reported for graphene exfoliated in NMP (~ 5 S/m) [7] and lesser than that of graphene dispersion filtered on Nylon membrane reported in our previous work [25], graphene dispersed in ethanol (~ 1130 S/m) [11] and graphene prepared by ball milling method (1200 S/m) [26]. This decrease in electrical conductivity of multi-layer graphene from that of few-layer graphene/single-layer graphene is attributed to the reduction of surface channels and increase of inter-layer channels, which diminishes the overall mobility of the conduction electron [25]. The sheet resistance is very low compared to that of graphene produced by soft transfer printing method (0.3–17 k Ω /sq) [27] and dip-coated graphene (4.7 k Ω /sq) [14] and rGO (11–37 k Ω /sq) [28]. This appreciable electrical conductivity of spray-coated liquid phase exfoliated graphene thin film, compared to that of graphene thin films prepared by other solution processes, suggested that it can be used in solar cells and fuel cells as a counter electrode instead of platinum/molybdenum electrodes.

The photoconductive response of the graphene thin film was taken in dark and illumination conditions. The electrical contact of the deposited film was prepared with 0.5 cm spacing by silver coating using the thermal evaporation technique. Then it was connected in series with a KEITHLEY 485 Pico ammeter and DC power supply (Fig. 7a). Subsequently, the graphene film is illuminated with a full spectrum of the 60 W xenon lamp. The DC input was increased from -5 to $+5$ volts in steps and subsequent dark currents and photocurrents were measured using the electrometer [29].

The noted linear I - V curve of the film in Fig. 7b discloses the Ohmic nature of the contact and good photoresponse of the graphene film after illumination. This result is due to the stimulation of more quantity of photoelectrons from the liquid phase exfoliated graphene film under illumination. Remarkably, the photocurrent of graphene film is ~ 5 times higher than that of the dark current. This result is well-matched with that of reduced graphene oxide/reduced graphene oxide quantum dots hybrids film [30]. It is observed that the good optical absorbance and electrical properties of the film kindle the good photoresponse of the sample.

4 Conclusion

Homogeneous MLGF prepared by spray pyrolysis technique shows moderate optical transparency of 57%, electrical conductivity of ~ 744 S/m and sheet resistance of 3.54 k Ω /sq. Hence, this simple and cost-effective technique can be applied for large scale production of graphene thin film with high electrical conductivity and optical transparency as a better replacement for ITO in various applications after optimizing the synthesis parameters of graphene dispersion and thickness of the thin film. By increasing the ultrasonication time the thickness of the graphene sheets can be reduced and there by the optical and electrical properties of the graphene thin film can be improved. Deposited liquid phase exfoliated graphene thin film also showed better photoconductive property. Hence, the obtained results implied that graphene thin film prepared using facile chemical spray pyrolysis of liquid-phase exfoliated graphene dispersion can be employed as a reliable candidate in optoelectronics devices.

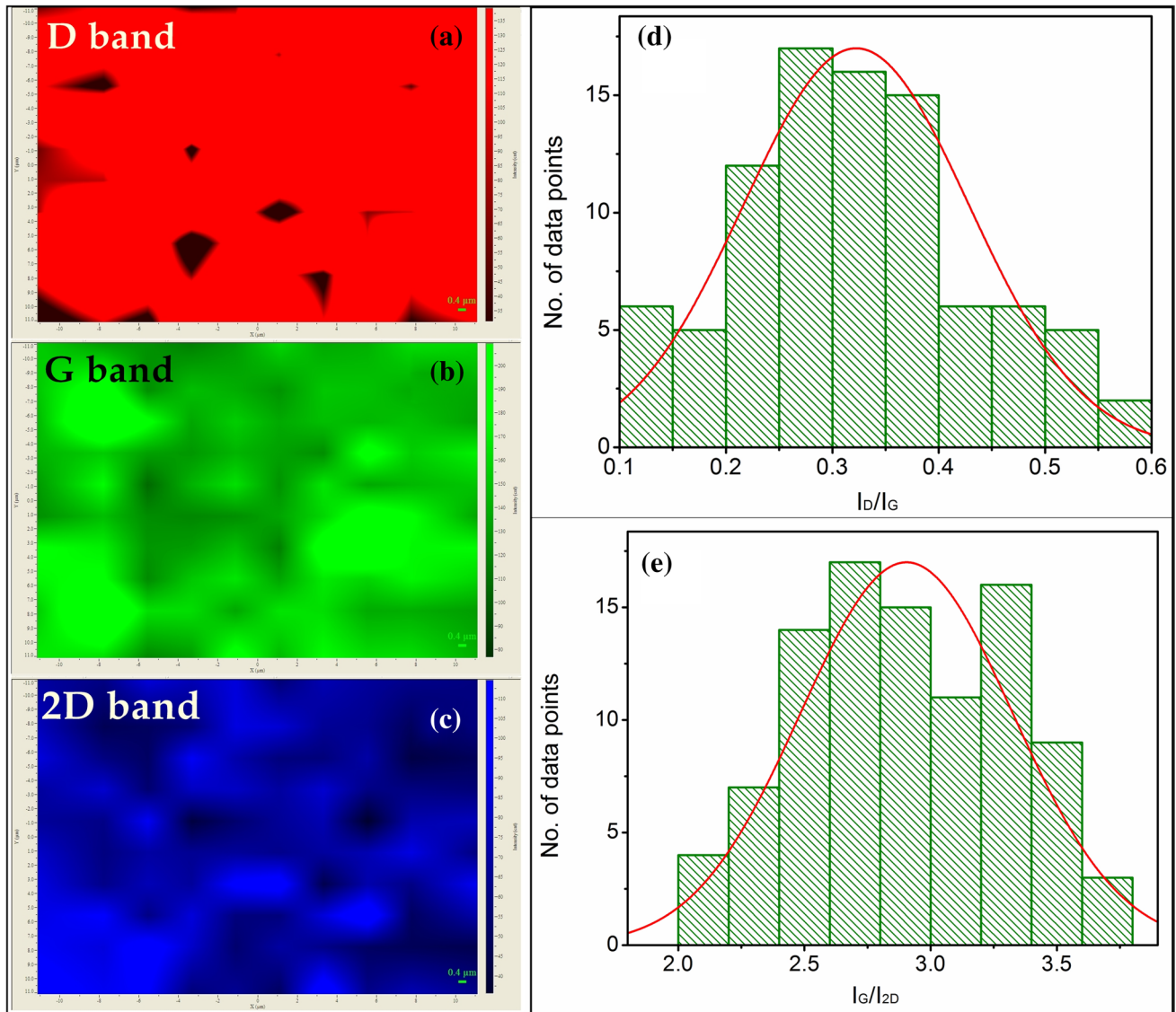
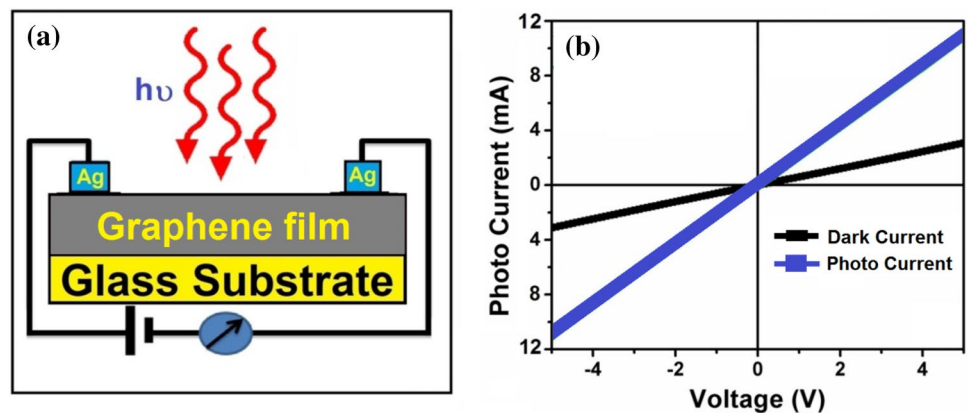


Fig. 6 (a–c) Raman intensity mapping images of D, G and 2D bands and (d, e) corresponding I_D/I_G ratio and I_G/I_{2D} ratio of graphene thin film

Fig. 7 (a) I – V setup for photoresponse measurement, (b) I – V curve for dark and under illumination condition for graphene film



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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

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