The study of wettability in reduced graphene oxide film on copper substrate using electrostatic spray deposition technique

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Abstract. We report the preliminary study of wettability properties of reduced-graphene oxide (rGO) film prepared by electrostatic spray deposition technique. Wettability is an important property in surface material that can drive the direction of development for various applications. The experiments were performed using copper plate as substrate and graphene oxide (GO) solution of 4 mg/ml as coating material. We examined and investigated the effect of various high voltages to surface morphology and wettability of rGO. The voltages are varied at 1.0 and 1.5 kV and substrate temperature was fixed at 150°C. The rGO film was obtained through thermal treatment of GO film at 200°C for 1 hour. The surface morphology of rGO films were examined using optical microscope and scanning electron microscope. The wettability was examined using static contact angle method to determine water contact angle. The results show that the surface roughness and water contact angle of rGO film was affected by deposition voltage. The highest water contact angle of rGO film of 123.98° that indicated good hydrophobic properties was obtained for deposition condition on 1.5 kV.

1. Introduction

Graphene sheet is the thinnest material in the world. It is known as 2D organic material and has many superior properties such as highest thermal conductivity [1], highest transparency [2], highest electric conductivity [3] and highest mechanical properties [4]. Therefore, graphene is a promising material for many applications including boiling heat transfer. The previous study reported that mixed-wettability of hydrophobic-dot and superhydrophilic material are able to enhance heat transfer performance [5], and shown an unique bubble behavior on subcooling condition [6]. Recent studies show that reduced graphene oxide (rGO) as heater and working fluid increases the value of heat transfer coefficient (HTC) and critical heat flux (CHF) [4]. The same result was also found by An et al. [7] by using supersonic spraying technique of rGO films. The surface imperfection is characterized by rGO flakes structure as a factor affecting bubble or bubble nucleation [5]. Several studies have shown that the surface morphology of graphene coating influence the surface wettability that is indicated by changing of water contact angle (WCA). Number of graphene layers have shifted the wettability [8]. Thermal treatment also affects the value of wettability [6]. With increasing thermal annealing of GO/TiO$_2$ coating, the value of WCA is increased. Uniquely, the shift in wettability properties from
superhydrophobicity having the value of WCA larger than 150° to superhydrophilicity that the maximum value of WCA is 5° may occur due to the effects of UV irradiation and wettability values can be reversible by the heat treatment process. Environmental factors also affected the value of wettability of graphene coating. When graphene coating binds water molecules from the environment then the wettability value shifts from hydrophobic (WCA > 90°) to hydrophilic (WCA < 90°) [9]. Providing high quality of rGO with good hydrophobic properties become one of big challenges. Some researchers reported preparation of rGO by spraying technique with various improvement such as supersonic spraying [7], substrate temperature assisted [10], superhydrophic assisted [11], and electrostatic [11, 12]. Here, we reported the synthesis of rGO thin film by electrostatic spray deposition and studied the effect of electrostatic high voltage condition to its morphology and wettability properties in rGO thin film.

2. Experiment Method
A commercial graphene oxide (Graphenea) was used as GO water solution sources with concentration of 4 mg/ml. The GO solution was stirred using magnetic stirrer for 30 minutes then sonicated for 30 minutes at room temperature using ultrasonic bath. A subsection samples substrate was made from pure copper plate (Nilaco: 113519) with size 1 cm x 1 cm without polished treatment. The copper surface was cleaned by acetone prior to deposition of GO films. The deposition of GO film was prepared by electrostatic spray deposition (ESD). The schematic ESD that utilized in this experiment is shown in figure 1. We use a copper wire ring with diameter (d) of 5 cm as a cathode and the nozzle of sprayer as an anode. The distance between electrodes was 7.5 cm and the distance of an anode to substrate in hot plate (H) was 10 cm. GO solution is injected and controlled using micrometer staging that fixed to the spray gun (Meiji F100) and connected to the compressor. GO aerosols are generated using high pressure of 8 bar and adjusted the nozzle sprayer to get the desired aerosol size. The copper substrates are cleaned using standard procedure prior to deposition of GO film. High voltage source can be adjusted from 0 to 2 kV. In this report, ESD was adjusted to be 1.0 kV and 1.5 kV. Hot plate temperature was fixed to 150° C as temperature of substrate.

![Figure 1. Schematic of modified electrostatic spray deposition (ESD).](image)

The thermal treatment was used to obtain rGO films from GO films on Cu substrate as a result of electrostatic spray deposition. Samples of GO films on Cu substrate were heated at 200°C for 1 hour. All rGO films were characterized by optical microscope (Zeiss Axio imager 2) to define the homogeneity of rGO films in microscopic scale, static contact angle measurement to define the value of WCA and scanning electron microscope (SEM) to measure nanostructure of rGO films. Additionally, the energy dispersive spectroscopy (EDS) measurement was also performed to obtain the ratio of carbon and oxygen in rGO films. Static contact angle measurement is based on drop test of deionized (DI) water on the surface of rGO film at room temperature.
3. Results and Discussion
Surface images of rGO films on cupper substrate were performed macroscopically using an optical microscope with 100 times magnification as shown in figure 2(a) and 2(b) with electrostatic high voltage of ESD of 1.0 kV and 1.5 kV, respectively. The surface area of each image is 880 µm × 660 µm. Both images have different contrasts and gray level distribution indicated the presence of different surfaces homogeneity and roughness. It can also be seen that size of rGO films are unequally distributed but rather form a spotted pattern indicated the surface rGO films more rough. Figure 2(b) has a brighter contrast indicating that the sample deposition using high voltage of 1.5 kV is thicker than that of deposited using a voltage of 1.0 kV.

![Figure 2](image)

**Figure 2.** Surface images of rGO films on Cu substrates deposited using electrostatic high voltage condition of (a) 1.0 kV and (b) 1.5 kV.

Further evaluation to figure 2 can be based on 2.5D surface profile as shown in figure 3. Figure 3(a) and 3(b) represent surface profile of sample film deposited at high voltage condition of 1.0 kV and 1.5 kV, respectively. For comparison, surface profile of bare copper was also displayed in figure 3(c). From figure 3(c), it can be observed that the bare substrate has a homogeneous surface profile indicated by no contrast difference. The bare substrate itself indicated to have black contrast. Figure 3(a) for sample deposited with 1.0 kV has a coarser surface profile, which is indicated by contrast differences and has patterns forming steep peaks indicating by a spotted pattern small and tight spot. Figure 3(b) shows surface profile with large spot. It is also found that the intensity of the top of image in figure 3(a) has higher intensity than that of the top in figure 3(b). Both of images are caused greater stresses resulting in cone-shaped when spraying becomes sharper with the same droplet volume. The coverage area will be larger and thicker addressed by the spraying result with the larger voltage having a larger spot pattern and higher intensity [13].

![Figure 3](image)

**Figure 3.** 2.5D surface profile of rGO films on Cu substrates deposited using electrostatic high voltage condition of (a) 1.0 kV, (b) 1.5 kV and (c) Cu bare surface.

The WCA testing was performed by droplet dripping DI water with a volume of 12 µL on the sample surface of rGO film deposited using high voltage condition of 1.0 kV, 1.5 kV and Cu bare as seen in this figure 4(a), (b) and (c), respectively. There is evolution of contact angle from 77.88° of WCA for Cu bare to 123.98° of WCA for 1.5 kV rGO film. The value of WCA has good correlation with the roughness on the sample surface. Increasing the WCA value will increase roughness on the
sample surface. Samples deposited with 1.0 kV has greater water contact angle of 103.05° than that of the Cu substrate bare of 77.88° because of the contribution of surface coarseness. However, an increasing in WCA of samples deposited with 1.0 kV and 1.5 kV stresses occurs due to the morphological differences of the repositioned rGO layer. The rGO film deposited with a voltage of 1.5 kV has a greater roughness. This result can be explained using a dynamic molecular simulation where the height of roughness gives the dominant effect of the roughness of a surface [8]. From WCA values of rGO films, it is found that both samples of rGO films deposited using electrostatic high voltage of 1.0 kV and 1.5 kV have hydrophobic properties.

Figure 4. DI water drop test contact angle of rGO films on Cu substrates for electrostatic high voltage condition of (a) 1.0 kV, (b) 1.5 kV and (c) Cu bare surface.

The SEM imaging results of rGO samples deposited using 1.0 kV and 1.5 kV are shown in figure 5. The rGO flake is identified as wrinkled pattern on the image which is pointed by the bold black arrow. Figure 5 shows two magnifications for each sample that are magnification of 5000 (figure 5(a) and 5(b)) and 30000 (figure 5(c) and 5(d)). It is clearly visible in figure 5(a) a collection of rGO flakes deposited above substrate but not covering the entire surface of Cu substrate formed a pattern spoted. With larger magnification of the square dot line area, it is clearer that rGO flake has not deposited flatly. Some parts are making up its own cluster and contribute to its surface roughness. In contrast to samples deposited with 1.5 kV, SEM imaging of 5000 times magnification for this sample has not visible substrate surface indicating the deposition covers all areas. There is a cluster forming section as seen in the enlarged area with square dot line of figure 5(c).

Figure 5. SEM images of rGO films on Cu substrates deposited using high voltage condition of 1.0 kV with (a) 5000 times magnification, (b) 30000 times magnification, (c) rGO film with 1.5 kV with 5000 times magnification and (d) 30000 times magnification.

The height of the cluster formed in this sample is due to the effect of increasing electrostatic voltage during deposition as has been discussed previously in the 2.5D surface profiles. The same position pointed by an arrow in the square dot line was analyzed using EDS to justify the existence of rGO flakes. Sample tested was sample deposited using 1.0 kV. It is found that the film composition was consist of Carbon (C) of 39.72%, Oxygen (O) of 10.34% and Copper (Cu) of 49.95%. Since the value of 49.95% of Cu element is belong to the Cu substrate, normalized composition of rGO film found the
percentage value of C to be 79.35% and O to be 20.65%. The composition of commercial GO, the presentation value of C was 49.56% and O was 41.50%. It is clear that in our sample, the ratio of C/O was 3.84, while for commercial GO, the ratio C/O was 1.15. In addition to the morphology, this deposited material type will also affect the WCA value. GO material has a smaller surface tension than rGO material. This result is in good agreement with modeling study by Perrozia et al. [14].

4. Conclusions
Deposition of rGO film by electrostatic spraying technique has successfully prepared with electrostatic high voltage condition of 1.0 kV and 1.5 kV. The rGO film deposited using electrostatic high voltage of 1.5 kV, has highest value of WCA and roughness. It is found that increasing in WCA value of samples deposited with 1.0 kV and 1.5 kV was due to the morphological differences of the repositioned rGO layer. WCA values of rGO films deposited using electrostatic high voltage of 1.0 kV and 1.5 kV were 103.05° and 123.98°, respectively, indicating that both samples of rGO films have hydrophobic properties.

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References
[1] Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 Nano Letter 8 902
[2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197
[3] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666
[4] Lee C, Wei X D, Kysar J W and Hone J 2008 Science 321 385
[5] Suroto B J, Tashiro M, Hirabayashi S, Hidaka S, Kohno M, Takata Y 2013 Journal Thermal Science and Technology 8 294
[6] Shen B, Suroto B J, Hirabayashi S, Yamada M, Hidaka S, Kohno M, Takahashi K and Takata Y 2015 Applied Thermal Engineering 88 230
[7] An S, Kim D Y, Lee J G, Jo H S, Kim M W, Al-Deyab S S, Choi J, Yoon S S 2016 International Journal of Heat and Mass Transfer 98 124
[8] Wei N, Lv C and Xu Z 2014 Langmuir 30 3572
[9] Shen B, Yamada M, Orejon D, Suroto B J, Hidaka S, Kohno M, Takahashi K and Takata Y 2015 Formation of air-rich bubbles on a superhydrophobic surface in sub cooled boiling (9th International Conference on Boiling and Condense Heat Transfer)
[10] Woo J S, Lee G W, Park S Y and Han J T 2017 Thin Solid Films 638 367
[11] Wang L J, Li L, Yu J, Wu Y, He H, Ouyang X, Zhao X, Yen Y C and Lee L J 2014 Carbon 79 294
[12] Wilhelm O 2005 Electro hydrodynamic spraying–transport, mass and heat transfer of charged droplets and their application to the deposition of thin functional films (Zurich: Dissertation at Swiss Federal Institute of Technology)
[13] Wang Z H, Wang F P, Fan J R, Gao Q J and Wang J Q 2016 Journal of Engineering and Technology Research 8 31
[14] Perrozia F, Crocea S, Treossi E, Palermo V, Santuccia S, Fioravantia G and Ottaviano L 2014 Carbon 77 473