

# Contact Angle Dynamics during the Evaporation of Water from Hydrophilic and Hydrophobic Graphene Surfaces

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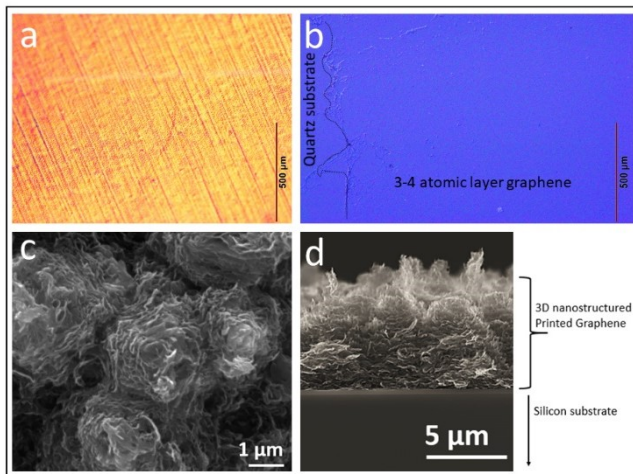
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Evaporation of droplets from surfaces is an important phenomenon in thermal management (e.g., integrated circuits, power electronics, lasers [1]) as well as applications such as biosensing, anti-fouling surfaces. Additionally, evaporation from porous media is an important component of the Food, Energy, and Water Nexus, particularly regarding water loss from soils; different soil additives and wettabilities can affect overall evaporation rates. Previous research identified concentration gradients [2], droplet pinning/contact line dynamics [2-3] and droplet contact areas and contact angles [4] to be important parameters governing the evaporation of water from surfaces and thereby affecting heat transfer [1]. However, despite graphene's well-documented electrical, mechanical, optical, and thermal properties, evaporation from different graphene surfaces has not been well investigated.

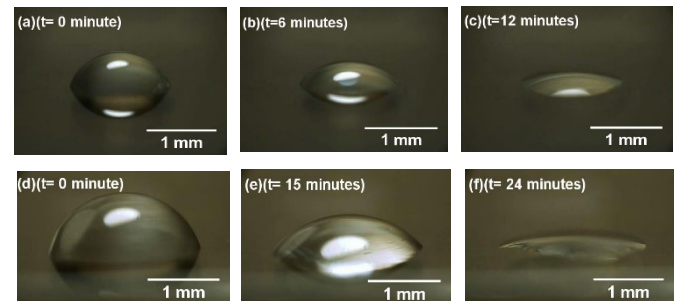
For this experimental study on evaporation of water from graphene, two graphene samples with different thickness and microstructure were used. Figure 1 shows the representative optical and scanning electron microscope (SEM) images of the two samples. Sample 1, shown in Figure 1a-b, is a 3 to 4 atomic layer of continuous graphene sheet grown on copper substrate via chemical vapor deposition (CVD) and was subsequently transferred to a quartz substrate using a wet chemical method reported previously [5]. The graphene thickness is at 1.2 nm to 1.4 nm, as measured by Atomic Force Microscopy. Sample 2, shown in Figure 1c-d, represents an inkjet-printed reduced graphene oxide on silicon and subsequently treated with a direct pulsed laser writing (DPLW) process for surface 3D-nanostructuring. The layer thickness is between 6  $\mu\text{m}$  and 7  $\mu\text{m}$ . This nanostructuring technique is of

interest for heat transfer, electrochemical sensors [6], and bioelectronics actuators. As demonstrated in Figure 1, the DPLW-enabled printed graphene includes a unique surface topography. While a printed graphene is hydrophilic, DPLW-enabled printed graphene, using a laser energy above a critical value, shows hydrophobic characteristics.

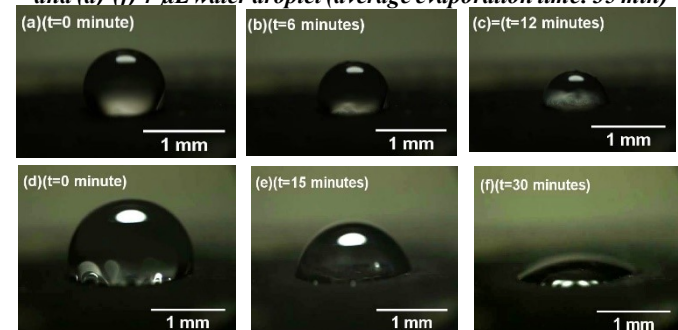
This research investigates evaporation of sessile deionized water droplet from two different graphene samples. Two droplet volumes (i.e., 1 and 4  $\mu\text{L}$ ) were placed on graphene using a 0.2-2  $\mu\text{L}$  pipette. Quiescent experiments were conducted in a controlled environmental chamber. Conditions were maintained at a set pressure ( $P=1$  atm), temperature ( $T=20^\circ\text{C}$ ), and 60% RH. A cool LED lamp was used to provide sufficient lighting. Evaporation phenomena were captured using a high-speed camera (Fastec Motion Controller) at 24 FPS; evaporation times were recorded. The captured files were processed with PFV software; side views are presented in Figures 2 and 3.



**Figure 1.** (a)-(b) Graphene sample 1 grown by CVD and chemical etching (hydrophilic) and (c)-(d) graphene sample 2 created through direct pulsed laser writing (hydrophobic)



**Figure 2.** Evaporation from the hydrophilic graphene surface: (a)-(c) 1- $\mu\text{L}$  water droplet (average evaporation time: 16 min) and (d)-(f) 4- $\mu\text{L}$  water droplet (average evaporation time: 35 min)

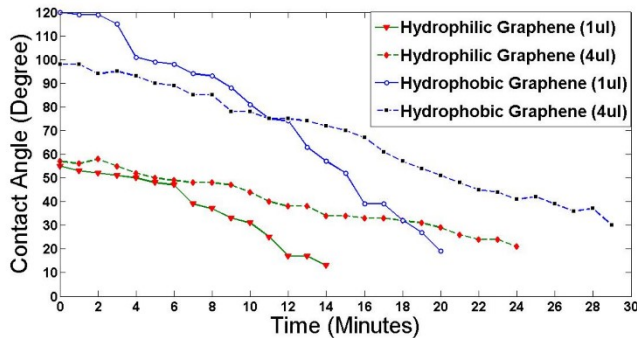


**Figure 3.** Evaporation from the hydrophobic graphene surface: (a)-(c) 1- $\mu\text{L}$  water droplet (average evaporation time: 21 min) and (d)-(f) 4- $\mu\text{L}$  water droplet (average evaporation time: 38 min)

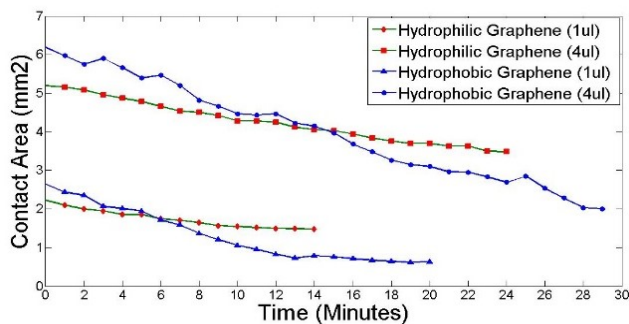
For both graphene surfaces, the experiments were replicated twice for each droplet volume. Due to a lower contact angle, water droplets were more stretched on the hydrophilic graphene compared to the hydrophobic graphene [Figures 1 and 2, (a) and (d), resulting in a larger air-water interfacial area. On average, 1- and 4- $\mu\text{L}$  water

droplets fully evaporated in 16 and 35 mins, respectively, from the hydrophilic graphene surface. From the hydrophobic graphene, 1- and 4- $\mu$ L water droplets fully evaporated in 21 and 38 minutes, respectively. Droplets evaporated at a faster rate from the hydrophilic graphene samples.

Figures 4 and 5 show the variation of contact angles and areas with time evaporation of water droplets from two different graphene samples. For the DPLW-enabled printed graphene surface, the initial contact angles are 120° and 98° for 1- and 4- $\mu$ L water droplets, respectively. For the CVD graphene on quartz surface the initial contact angles are 55° and 57°. The contact angle evolution depends on droplet size and surface; contact angles decrease in an approximately linear rate for the 4- $\mu$ L droplets.



**Figure 4. Variation of contact angles with time for 1- and 4- $\mu$ L water droplets on hydrophilic and hydrophobic graphene surfaces**



**Figure 5. Variation of contact areas with time for 1- and 4- $\mu$ L water droplets on hydrophilic and hydrophobic graphene surfaces**

Contact angle, radius, and area are important parameters governing evaporation. Figure 5 depicts the variation of contact area with time. Contact area was calculated using the method developed by Yu et. al. [7]. The relation among contact radius  $r(t)$ , droplet height  $h(t)$  and contact angle  $\theta(t)$  is shown in equations (1)-(2). Droplet evaporation can be classified into three stages: CCR (Constant Contact Radius), CCA (Constant Contact Angle), and mixed mode. In this work, for the hydrophilic graphene surface the contact area slowly decreases with time and the contact angle more rapidly reduces with time; approximately the opposite happens for hydrophobic surface. For the two different cases, the variation of contact area can be illustrated by equations (3) and (4).

$$\begin{aligned} & \text{[Redacted]} \quad (1) \quad \text{[Redacted]} \quad (3) \\ & \text{[Redacted]} \quad (2) \quad \text{[Redacted]} \quad (4) \end{aligned}$$

From Figure 5, the contact areas of water droplets (1- and 4- $\mu$ L) decline slowly and in a linear fashion during evaporation from the hydrophilic graphene surface. The contact radius of droplet on

hydrophilic graphene surface remains generally constant with time, but the droplet height rapidly decreases with the decreasing contact angle. For the hydrophobic graphene surface, the contact areas decreased at a faster rate than for evaporation from the hydrophilic surface. Interestingly enough, during evaporation from the hydrophobic graphene surface, there were instances where the contact area increased with time (e.g., 0–6 min and around 25 min). This phenomenon has been observed by Maroo et. al [8] for boiling heat transfer. They illustrated that nanostructured materials, such as graphene, have pores among their layers and water can spread due to these small pores. For this reason, though the DPLW printed graphene generally functions as a hydrophobic surface on the macroscopic scale, it is hypothesized that the presence of nanostructured pores instigates spreading of the water droplet, thereby explaining the observed increase in contact radius and area during evaporation.

Wettability and contact angle dynamics play a vital role in characterizing evaporation from two different types of graphene (i.e., hydrophilic and hydrophobic). This research analyzes contact angle dynamics and contact area changes for water on two different graphene sample during evaporation. Further research would further investigate these phenomena, particularly the role of small graphene pores on water spreading.

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