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Self-assembly by multi-drop evaporation of carbon-nanotube droplets on a polycarbonate substrate

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HIGHLIGHTS

- A new low-cost procedure to fabricate nanoporous nanostructures is proposed.
- A CNT network is obtained on a polycarbonate substrate via multidrop evaporation.
- The nanostructures are characterized by scanning electron microscopy.
- A considerable decrease in electrical resistance and contact angle is observed.
- High efficiency is observed for a relatively simple procedure.

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ABSTRACT

Carbon nanotubes are allowed to self-assemble by depositing a droplet of a water dispersion thereof and letting it evaporate on a polycarbonate substrate. The effect of the number of droplets, evaporated on the same deposition spot, on the self-assembly density is assessed to be more than proportional for the first five depositions. The obtained nanoporous nanostructures are further tested for their electrical resistance and wettability. Two concentrations are used. It is found that a higher concentration and more importantly a higher number of droplet depositions causes the electrical resistance to decrease up to four orders of magnitude and the static contact angle to decrease more than three times. The contact angle hysteresis also increases due to an increasing advancing contact angle and a decreasing receding one. This is explained by the degree of coverage of the substrate by the carbon nanotubes as is also shown by scanning electron microscope images. A better coverage is suggested to cause more pinning for an advancing droplet and a higher capillary force for a receding droplet.

1. Introduction

Self-assembly has many applications. It is applied in the medical sector [1]. It can also be used for energy storage [2] or in membrane technology [3]. As a principle, the deposition of micro- and nanoparticles on a substrate is relevant for manufacturing different kinds of coatings [4], but also to prepare micro-and nanowires [5] and to deposit complicated organized biological structures, such as DNA [6,7]. There are several ways to achieve particle deposition, such as dip coating, sedimentation and electrostatic assembly. Convective deposition and more particularly drop evaporation are convenient ways to deposit micro- and nanoparticles [8]. The amount of fluid used is minimized, possibly inducing economic advantages, and the outcome can easily be controlled, by choosing initial parameters [9].

The interest lies in creating patterned structures out of evaporating drops, which can be of use for energetic and medical applications. The deposited patterns that are left by the evaporated colloidal drops can present a multiplicity of structures, such as the ring structure [10], a central bump [11], a uniform deposit [12], or more complex structures such as multiple rings [13] and hexagonal arrays [5]. This variety of patterns reflects the multiscale attractive forces and transport phenomena taking place during the droplet evaporation. As for the fluid dynamics, several mechanisms play an important role, depending on whether a droplet is deposited directly on the substrate or dropped from a certain height. If droplet impact is associated, the fluid dynamics

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are determined by the Reynolds and Weber number of the droplet impact [9], as well as the impact angle, interfacial deformation or break-up. Marangoni forces, wetting characteristics and evaporation at the free surface are other types of mechanisms that influence the fluid dynamics. The heat transfer, not only associated with the evaporation (cooling) but also with conduction from the substrate, is coupled to the fluid dynamics and the two influence each other in a complex manner. Mass transfer also occurs, either by diffusion of the vapor of the liquid around the drop, by convection-diffusion of particles in the drop or by particles interactions with the substrate surface. If the radial flow is strong, it will carry particles towards the pinned wetting line, where evaporation is the highest, forming the so-called coffee-ring [10,14]. If thermal Marangoni forces are more important, a particle accumulation can take place around the center of the evaporated drop [15]. Uniform depositing can also occur by self-assembly [12,16]. It is worthy to note that the interaction between the particles and the substrate can play an important role in the final shape of the patterns [16].

Self-assembly in evaporating nanofluid droplets has already been investigated and has been reasonably well investigated [17–21]. However, the methods used in these studies can demand for a high concentration of nanoparticles in the deposited droplets. Although a certain tendency to agglomerate is beneficial to the self-assembly process, this can lead to too much aggregation of the particles even before they adhere to the substrate. A great part of the self-assembly can thus take place in the liquid leading to agglomerates of different uncontrollable sizes, which causes uneven layers of particles on the substrate. In order to avoid this, the concentration should be low. However, this would lead to insufficient coverage of the substrate. A solution to this problem is self-assembly by evaporating multiple nanofluid droplets at the same place, one after the other. Although, this is a promising solution, it is still an open field, and the subject of this paper. Before any theoretical or parametrical work can be performed, we need first to have an idea of how the particle self-assembly affects some material properties that are of large interest: we choose to measure experimentally the electrical resistance and the wetting behavior through the static contact angle as well as the advancing and receding contact angles (contact angle hysteresis). The nanofluid in this paper is a dispersion of carbon nanotubes in water with two different concentrations, and the droplets are deposited on a polycarbonate substrate. In order to understand better the observed behaviors, the nanofluid and deposited nanotubes are respectively characterized by particle size distribution and scanning electron microscopy. This work should also give some insight on whether a certain wetting behavior or electric conduction can be attained by either changing the nanofluid concentration or rather by changing the number of evaporated droplets containing that same nanofluid.

2. Experimental

2.1. Multi-drop setup and self-assembly process

We propose to perform our multi-drop experiment by depositing droplets that contain nanotubes and let them evaporate at room temperature. The Marangoni instability in the droplet is rather strong for the dimensions used in this work (25 µl) [22] and we can expect that at these dimensions the motion in the droplet will be triggered as soon as the droplet is deposited. This implies that the timescale of droplet spreading, t_{spr}, (we have deposited the droplet in such a way as to avoid splashing, so that only the spreading phenomenon is of importance here) should be in the same order of magnitude as or smaller than that of thermocapillarity, t_{Ma} (Marangoni effect). The thermocapillary (Marangoni) timescale can be obtained from the definition of the Marangoni number $Ma \equiv \frac{\sigma_T r \Delta T_\perp}{\mu\kappa} \equiv \frac{\tau_{th}\tau_{visc}}{\tau_{Ma}^2}$. Here, σ_T is the temperature-induced surface tension gradient (typically, but not always, a negative number, but we will take the absolute number here for the purposes of this work) along the droplet's surface. Furthermore, r is the droplet radius, $\Delta T_\perp$ is the global temperature difference along the droplet's surface (perpendicular to the evaporation direction), μ is the dynamic viscosity ($\mu = \nu\rho$, with ν the kinematic viscosity and ρ the density) and κ is the thermal diffusivity. Using the usual thermal and viscous timescales, the thermocapillary timescale can be easily found to be

$$t_{Ma} = \sqrt{\frac{\rho r^3}{|\sigma_T|\Delta T_\perp}}. \tag{1}$$

The timescale of droplet spreading is taken from [23]:

$$t_{spr} = \sqrt{\frac{\rho r^3}{\sigma}}. \tag{2}$$

We can extract from this the ratio $\frac{t_{Ma}}{t_{spr}} = \sqrt{\frac{\sigma}{|\sigma_T|\Delta T_\perp}}$. Using material properties for water ($\sigma = 7.28*10^{-2}$ N/m [9] at ambient temperature and $\sigma_T = -1.54*10^{-4}$ N/mK [24]) give the value $\frac{t_{Ma}}{t_{spr}} \approx \frac{22}{\sqrt{\Delta T_\perp}}$. Typically, for evaporating water droplets, $\Delta T_\perp = O(1)–O(10)$ K [25], so that typically $\frac{t_{Ma}}{t_{spr}} = O(1)–O(10)$. This means that the Marangoni timescale is estimated to be of the order of magnitude of that of the droplet spreading or one order larger. Therefore, we can state safely that Marangoni instability will be triggered as soon as (just for information, Eq. (1) gives us an estimation of the Marangoni timescale for a 25 µl droplet: $t_{Ma} \approx O(10^2)$ ms) or shortly after the deposition of the droplet ($t_{spr} \approx$ 13 ms). Pattern formation induced by the Marangoni mechanism will therefore not be so much influenced by droplet spreading. After deposition, the nanotubes will then move along and create a certain pattern on the substrate after the evaporation process. Single drop evaporation has been studied previously [9]. In this work, we continue to deposit another droplet on the same spot, which evaporates again. This is repeated several times. In this way a certain self-assembled structure is obtained. We use two concentrations for our nanofluid: 1 and 2 g/l. Fig. 1 shows a picture of the multi-drop experiment, where 17 spots for droplet deposition are available one next to another. So, we will have nanotube depositions by evaporating one nanotube-containing droplet on the first spot, two on the second spot, three on the third one, …, up to seventeen on the seventeenth spot.

The position of the droplet is controlled by a motor with a precision of 0,01 mm. The droplets are deposited by a syringe with a size such that it creates droplets with a volume of 25 µl on “elevated spots” on the polycarbonate substrate with a diameter of 6 mm. The droplets are deposited on these elevated spots to create

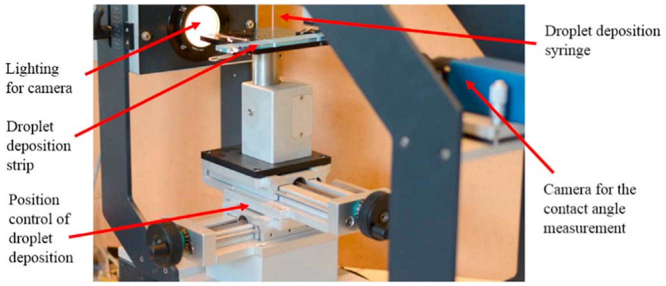

Fig. 1. Picture of the multi-drop experimental setup with seventeen droplet deposition spots on a deposition strip (see Fig. 5).