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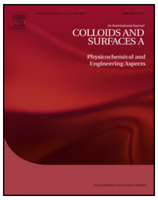


Depletion of carbon nanotube depositions and tube realignment in the spreading of sessile drops

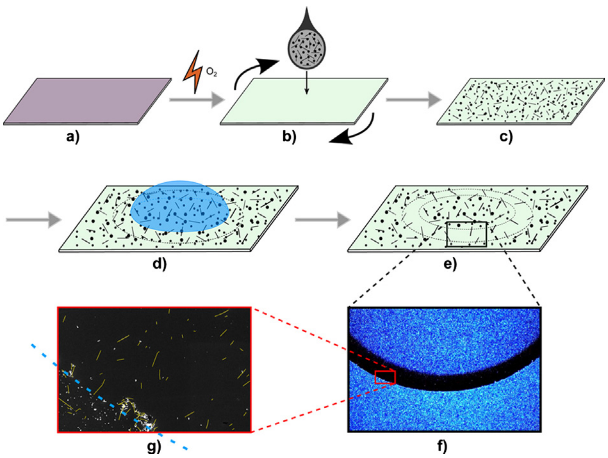
Matti J. Hokkanen[a], Roope Lehto[a], Jouni Takalo[a], Juha Salmela[b], Sanna Haavisto[b], Alexander Bykov[c], Risto Myllylä[c], Jussi Timonen[a,d], Markus Ahlskog[a,*]

[a] *University of Jyvaskyla, Department of Physics and Nanoscience Center, P.O. Box 35, FI-40014, Finland*
[b] *VTT Technical Research Centre of Finland Ltd., P.O. Box 1603, FI-40101 Jyvaskyla, Finland*
[c] *University of Oulu, Department of Electrical Engineering, P.O. Box 4500, FI-90014, Finland*
[d] *ITMO University, Kronverkskii ave. 49, 197101 Saint Petersburg, Russia*

HIGHLIGHTS

- We studied how the advancing contact line of a liquid drop interferes with multi-walled carbon nanotubes (MWNT) on a smooth silicon surface.
- Annular imprints were formed in the deposits, because of the evacuation of irregular carbon-based impurities by the mobile contact line.
- Many MWNTs remained in these annuli, but were re-oriented.
- A mobile contact line together with surface-chemical treatment of the substrate may thus provide means for improving or manipulating a nanotube deposit.

GRAPHICAL ABSTRACT



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ABSTRACT

We studied spreading of drops of water and dilute alcohol on multiwall carbon nanotube (MWNT) depositions. These deposits consisted of individual arc-discharge synthesized MWNTs and irregular amorphous carbon nanoparticles on hydrophilically rendered silicon substrates. The mobile circular contact line of a spreading drop created an annular shape on the deposit, where some of the MWNTs and the amorphous nanoparticles in particular were largely depleted. The effect was strongly dependent on the hydrophilicity of the substrate. Most of the MWNTs were not only left within the annuli, but were also apparently reoriented by their interaction with the passing contact line. Our results imply the possibility of applications in quality improvement of nanotube depositions in terms of both tube orientation and cleanliness.

1. Introduction

The methods and goals of modern research in nanotechnology, both fundamental and applied, have brought with them new

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[*] Corresponding author. Tel.: +358 40 805 4056.
E-mail address: markus.e.ahlskog@jyu.fi (M. Ahlskog).

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impetus and points-of-view to research on wetting phenomena. This is evident, for example, in the study of the diverse phenomena observed as nano-scale particles, usually dispersed in liquids, interact with interfaces or contact lines of liquid drops. Applications of wetting phenomena in nano-scale fabrication include techniques such as the deposition of nano-scale particles via the ‘coffee-ring effect’ [1], and alignment of high-aspect-ratio species via ‘molecular combing’ [2]. The coffee-ring effect and molecular combing are distinct processes, but they both relate to mobile contact lines of liquids. In the formation of coffee rings, small particles suspended in a drop accumulate at its outer perimeter in a ring-like fashion as the evaporation of liquid invokes outward hydrodynamic flows within the drop [1]. In molecular combing, rod-like micro- or nano-scale particles such as DNA [3] or carbon nanotubes [4] become aligned perpendicular to a receding contact line by the associated surface-tension force as they pass from a wet to dry environment. Furthermore, application of capillary forces for nano-scale fabrication and self-assembly processes also shows a lot of promise. For example, in the work by Duan and Berggren [5], nanocohesion induced by capillary forces was used to collapse nano-fabricated pillar structures into complex, self-assembled shapes.

Judging the developments so far, one can see two distinct issues that have been studied relatively poorly to date. One is that carbon nanotubes have been utilized only to a rather limited extent, the prime reason having been that they are not intrinsically dispersed in water. Their solubility can be achieved by functionalizing them with different molecular or polymeric substances, but at the cost of losing the most exciting properties of pure carbon nanotubes.

Another issue is that in the overwhelming majority of experimentally studied cases, the nano-scale particles have been dispersed within the drop and they have interacted with the interface from within the liquid (which is necessary if the aim is the deposition of nano-scale particles). Relatively little attention has been paid to the difference between the scenarios of nano-scale particles that encounter liquid contact lines from within or from the outside of the liquid. In geoscience, where colloidal particles in water sometimes play a role, the distinction is termed as that between drainage and infiltration [6].

The experiments done on molecular combing are all (at least nearly all) such that the nano-scale particles are within the liquid. The resulting orientation of 1D nano-scale particles, is necessarily affected by this factor, since the adhesion to the surface is usually radically different in the liquid and gas environments. It would thus be of interest to analyze also the case, in which an advancing contact line encounters a particle adhered onto the dry substrate, that is, on the outside of the liquid. If the particle is a carbon nanotube randomly deposited onto the surface, its angle with respect to the liquid interface can vary between 0 and 90°. This is expected to have an effect on the magnitude of the interfacial force [7], and hence there may be a systematic reorientation effect in the case of a well-defined contact line interacting with a carbon-nanotube deposition.

The mobile contact line is a familiar feature of, e.g., a spreading drop. If there is no impeding matter, pure liquid drops spread spontaneously on hydrophilic surfaces. The classical model experiment deals with the behavior of a small sessile drop, defined by the contact angle, θ, and diameter, D, on an ideally smooth surface as shown in Fig. 2(a), such that its contact radius on the substrate, R, is smaller than the capillary length of the liquid, $R < \kappa^{-1}$. Since the late 1970s, it has been known that the spreading of these drops generally follow what is known as Tanner's law, with the contact angle $\theta(t) \propto t^{-3/10}$ [8], independent of the kinematics of the system [9,10].

In this article we report results of simple experiments on the interaction between an advancing contact line of a liquid drop with deposits of multi-walled carbon nanotube (MWNT) material. The arc-discharge synthesized MWNT material that we use, includes much of (less adhesive) amorphous carbon nanoparticles, which are an unavoidable by-product in the synthesis process. The MWNTs were deposited by spin-coating on pieces of Si wafer with a hydrophilic pre-treatment. On these samples, liquid drops (ultraclean water or dilute solutions of isopropyl alcohol) were let to spread, resulting in easily visible annuli caused by partial depletion of the deposition (debris particles in particular) from the region of drop spreading. Among the MWNTs remaining on the affected region, we see evidence of their reorientation in response to the spreading contact line. With hydrophobic instead of hydrophilic pretreatment, the drop spread much less, and the depletion annulus was not formed. Our results thus demonstrate in a relatively simple manner the interaction on a substrate between a liquid interface/contact line and nano-scale carbon particles.

2. Experimental

Fig. 1 shows the central steps of sample preparation and execution of the experiment (except for the imaging procedures). In this figure is schematically depicted how a piece of Si wafer is conditioned with the surface treatment (a), how the MWNT material is deposited on the surface (b, c), and how an expanding water drop placed on the surface results in the formation of an annulus in the deposit (d, e). A section of a typical annular interface is shown in close-up optical (f) and SEM (g) images.

We used arc-discharge-grown MWNT material as obtained from a commercial supplier. The material consisted of both MWNTs and irregular amorphous carbon nano-scale particles, in an average ratio of 20%/80%, as estimated with AFM from the depositions used in the experiments (Suppl. Inform.). The MWNTs had diameters typically in the range 10–20 nm, and lengths up to 2–4 μm. Their high aspect ratio separated them unambiguously from the rest of the material in the microscopy images we used here. The MWNT material was dispersed as received into dichloroethane (DCE). Unprocessed MWNTs are known to be hydrophobic in nature.

Preparation of the Si surfaces for the standard samples included an oxygen-plasma treatment in an RIE (reactive ion etching) equipment, which rendered them hydrophilic. In comparative experiments, the Si surface was made hydrophobic via immersion into a solution of hydrofluoric acid (HF). Alternatively, hydrophobic surface characteristics were obtained by evaporating a thin film of Au. A few drops of MWNT/DCE solution were spin coated on such carefully prepared pieces of Si wafer. A high-magnification SEM image of a pristine deposition is shown in Fig. 2(c).

The hydrophilic and hydrophobic surface-chemical treatments both have a limited effectiveness in time, with a substantial decay in their properties in a period of hours or days in a normal laboratory atmosphere [11]. In our experiments, we separately accounted for the effect of this decay by varying the time delay from the RIE treatment to the experiment.

The sessile-drop experiments, with water (millipore ultra pure) or a dilute (less than 10% by volume) water solution of isopropyl alcohol (IPA), were performed immediately after sample preparation. In a typical experiment, a micropipette was used to inject a drop of the liquid, typically 1.5–3.0 μl in volume, onto a MWNT-deposited sample, and then flushed away with a high-pressure jet of air after a given period of spreading time, usually 20 s. The annular imprints created by the drops in the MWNT deposits were characterized with a dark-field optical microscope, and some of them further with SEM and AFM.

Time evolution of the diameter and contact angle of the drop were captured using a high-speed camera mounted in a side-view perspective (Fig. 4(a) shows an example of the captured frames). ImageJ image-analysis software with the DropSnake