Superhydrophobic Nanowire Surfaces for Drop Movement Using Magnetic Fields

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ABSTRACT

We present a novel method to control water drop movement on superhydrophobic surfaces through magnetic fields. Water drops with paramagnetic particles can be moved on fractal Si-nanowire superhydrophobic surfaces at high speeds by displacing a magnet. A drop pinned to a surface defect can be combined with another drop containing paramagnetic particles thus allowing movement of the newly formed drop. A drop can also be split using two magnetic fields. Under a magnetic field, paramagnetic particles form chain-like clusters. The movement generating force appears as a consequence of chains pushing against the drop skin at the drop bottom, with chains acting as a lever and drop surface tension as a fulcrum. Our findings demonstrate the feasibility of using magnetic fields to move, combine and split aqueous drops on non-patterned superhydrophobic surfaces with the only driving force of magnetic fields, which appears as a promising way to manipulate small discrete amounts of water.

Keywords: microfluidics, droplet, magnetic field, superhydrophobic surfaces.

Controlling droplet movement under the influence of a stimulus is a capability of continued and growing interest. Although drop dynamic behavior on a super-hydrophobic surface is interesting from a scientific and technologic point of view, little is known about aqueous drops moving on a flat non-patterned superhydrophobic surface by mechanisms different from gravity. There are several examples of technologies that may benefit from key advances in this field, such as superhydrophobic surfaces capable of self-cleaning by the action of a rolling drop [1, 2] or microfluidics devices that take advantage of new effects and better performance derived from manipulating fluids at small scales [3]. Fascinating phenomena have been reported in the literature treating the dynamic behavior of non-wetting drops, mostly focused on non-moving drops dynamics on patterned non-wetting surfaces. Examples of these are the studies on the dynamics of drops rolling over an inclined superhydrophobic surface through the action of gravity [4, 5] or spreading on a flat, patterned superhydrophobic surface [6]. Relaxation and contact line dynamics have been studied in drops generated by drop-wise condensation on superhydrophobic geometrically patterned surfaces that grow until they become large enough to touch and coalesce [7]. Other studies used a water drop placed between a hydrophilic and a superhydrophobic patterned surface in order to measure fluid pressure effects on contact angle [8]. In previous work by our research group, we found that the contact angle of a drop on a superhydrophobic surface can be modified using light [9]. Digital microfluidics is an alternative paradigm for manipulation of discrete droplets, where processing is performed on unit-sized packets of fluid which are transported, stored, mixed, reacted, or analyzed in a discrete manner. This concept has already been demonstrated using electrowetting arrays for droplet transportation without the use of pumps or valves [10-12]. In this paper, we present a novel method to displace, coalesce and split paramagnetic-particle containing aqueous drops on flat, non-patterned Si nanowire superhydrophobic surfaces with the only driving force being the use of magnetic fields. By analogy with digital microfluidics by electrowetting, we name this phenomena digital magnetofluidics.

Over the past 70 years, pioneers such as Wenzel and Cassie and Baxter have made notable contributions to our understanding of surface wetting [13, 14] . Recently there has been a renewed interest in this subject and researchers have concentrated their attention on nanostructured materials, actuation of liquid contact angle changes using

external fields, and surface analysis measurements. A major goal in this area has been to control phenomena related to wetting such as capillary rise and fall and the movement of liquids along surfaces using an external stimulus such as light or electric fields. The interest in studies focused on water resides on the obvious ubiquity of the fluid and its importance in biomedicine and environmental studies. It was noted that even though plants can repel water using the so-called Lotus effect, the intrinsic contact angle of their leaves can be below 90 degrees. This effect was suggested to be non-ergodic since the same leaf can be fully wetted or non-wetted depending upon its history. An explanation for this phenomenon is that leaf surfaces feature roughness at multiple length scales [15]. This property can be mimicked to create artificial superhydrophobic surfaces [16]. When placed over a superhydrophobic surface, water drops tend to miminize their contact with the surface by becoming spherical, and tend to slide or roll off the surface extremely easily. The Lotus effect can be described by these three frames from one of the movies that we have recorded in our labs at ASU (Figure 1).

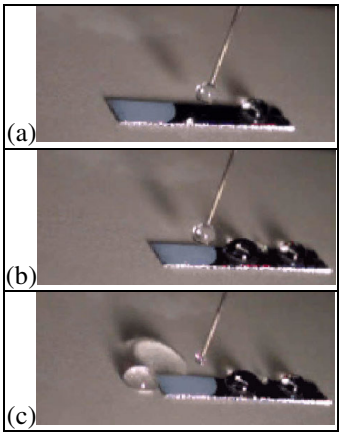

Figure 1: Three frames from a movie taken at ASU laboratories showing the difference between a hydrophobic and superhydrophobic surface. The left hand side of this silicon substrate contains nanowires while the right hand side does not. The entire surface is covalently coated with a fluoronated hydrocarbon. The water drops from the needle adhere to the right hand side of the sample while they slide off the left hand side of the sample.

Super-hydrophobic surfaces were prepared using vapor-liquid-solid (VLS) growth systems to create high aspect ratio Si nanowires with various diameters, spacing, and lengths. In order to create the hydrophobic effect, a perfluoronated hydrocarbon coating was covalently applied to the entire nanowire surface. The resultant superhydrophobic nanowire surfaces do not follow a simple geometric pattern and exhibit fractal, multidimensional, random roughness, with contact angles near 180 degrees [17]. The VLS growth technique employs small dots of gold that act as catalytic seeds for growing a high density of nanowires on a surface (Figure 2). During evaporation of a few monolayers of Au on a clean Si or glass surface, the Au self assembles into nanodots. In the subsequent VLS synthesis the Au dots form a eutectic liquid with Si from which liquid-mediated growth of single crystal Si nanowires occurs. The nanowire diameters are set by the Au dot diameters, with one-dimensional growth occurring as the AuSi eutectic dot rides along at the free end of the growing wire. The growth rate is linear in time and pressure, and the length of the nanowires is thus easily controlled by fixing the growth time. We note that the Au dots at the end of the nanowires account for only a very small area, and if desired, they can be chemically removed after growth.

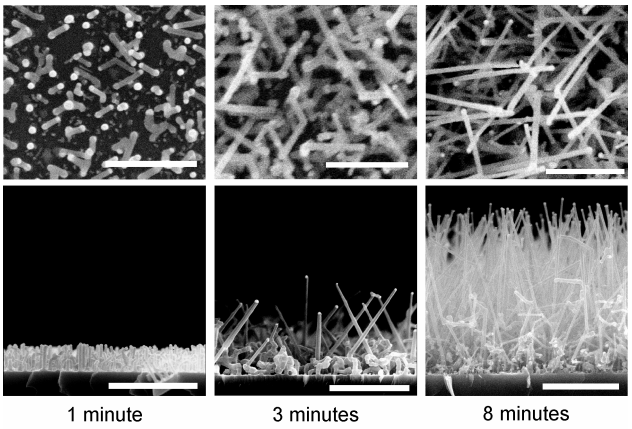

Figure 2: SEM images of nanowires grown on a Si (111) surface seeded with gold nanodots. After 8 minutes of growth a dense array of randomly oriented, long and thin silicon nanowires with gold caps is evident.

A small amount of paramagnetic particles was added to water drops, which were placed and held over a superhydrophobic surface sample by a permanent magnet located below the surface (Figure 3). We used Milli-Q water to prepare aqueous solution with different particle concentrations ranging from 0.1% to 5%. The spherical paramagnetic carbonyl iron particles used were acquired from Lord Corporation. The particles are highly polydisperse in size (ranging from 0.2 to 4.0 μm) and they have a high saturation magnetization (211 emu/g). The magnetic field was generated by a NdFeB bar magnet located below the superhydrophobic surface. To study the drop movement we shifted the magnet and recorded images with a CCD camera provided with a Navitar 12 x zoom system mounted from one side. We studied the effect of a magnetic field on drops with varied size and particle concentrations, and observed drop movement following the magnet movement from below in linear and circular patterns, for particle concentrations as low as 0.1% wt/wt, magnetic field intensity of 0.5 kGauss, and with speeds up to 7cm/sec along a 2 cm path (Figure 4).

Under the influence of the magnetic field, the particles form chain-like clusters [19]. The force that generates the movement appears as a consequence of the chains pushing

at the air-water interface climbing along the drop surface, with the chains as a lever and the drop surface tension as a fulcrum.

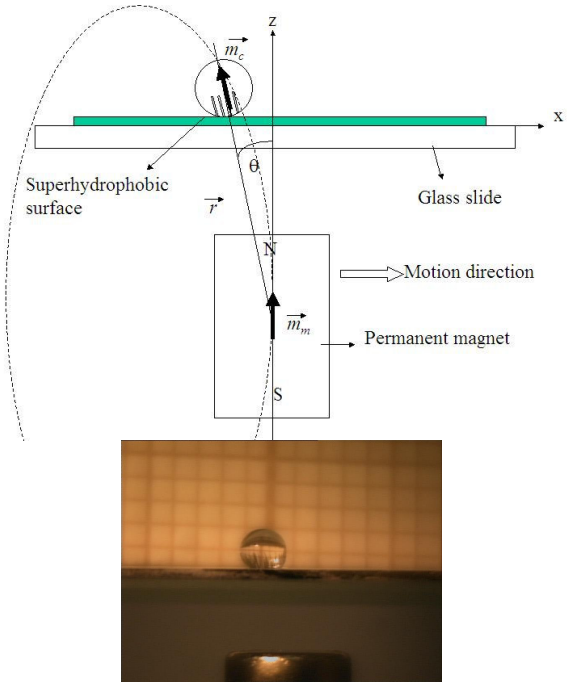

Figure 3. A schematic diagram and still image of a water drop containing aligned paramagnetic particle chains and a rare earth magnet, along with a picture of the experimental setup. The schematic illustrates a magnetic field line and the effect of geometry on the angle of paramagnetic particle chain alignment. The magnet is moved to the right and the drop slides along the superhydrophobic surface due to the parmagnetic particle chain's action pushing against the surface tension of the drop.

The movement of water drops on horizontal surfaces is due to the application of a magnetic field that aligns paramagnetic particles, attracts them to the magnet, and moves the drop of water in the process. The paramagnetic particle chains distort the shape of the drop at the bottom when the particles are attracted to the magnet. When the magnet moves the chain moves with it pushing against the "skin" or contact line of the drop due it surface tension. We believe that our imposed force is communicated at the contact line formed by air-liquid-solid phases. The water drop movement in our system occurs in the Cassie-Baxter, mostly non-wetted mode. With the larger-sized droplets that we have been studying it appears that the drop is sliding [5] which likely occurs due to the lack of significant frictional resistance since the wetted contact area is low. We observed that drop size for drops within the size range of 5-35µl does not affect the intensity of the magnetic field required to move drops on our hydrophobic surface, which suggests that frictional resistance is extremely low. These results are in accordance with molecular studies that predict roughness from the nano to the micro scale at the solid-liquid interface can greatly enhance slippage, probably due to the existence of bubbles at a nano-scale at the liquid-solid interface that influence slippage [18].

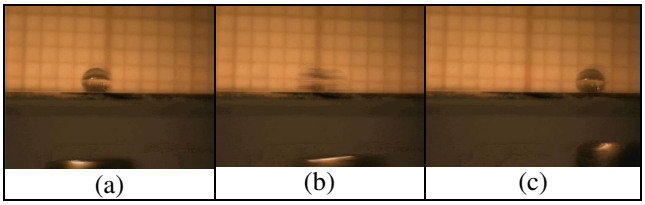

Figure 4: Sequence of 3 consecutive still images showing a millimeter-size drop with paramagnetic particles sliding on a superhydrophobic surface sample due to the magnetic field of a permanent magnet moving below the surface. The drop is displaced from position in (a) to (c) by the action of the magnet. Pictures were taken at 10 frames per second.

It is known that on inclined superhydrophobic surfaces smaller water drops actually roll down faster than larger drops which slide down the inclined surface [4, 5]. We have done several preliminary experiments to detect whether the drops in our system "slide" or "roll". Based on our observation of hydrophobic powders placed on top of 2 mm drops, we believe that drops of this size "slide" across the surface since the powders are not swirling even when the drops move at relatively high speeds. These drops are relatively large and they should slide when placed on an inclined superhydrophobic surface according to theoretical predictions [4]. The drop size dynamics transition point can be interpreted as depending in part upon the wetting transition between Cassie-Baxter and Wenzel wetting modes. Cassie-Baxter wetting assumes that the drop does not penetrate the valleys caused by the roughening of the surface, while Wenzel wetting assumes that the drop does penetrate completely. However, for smaller droplets where surface tension forces dominate over gravitational forces and when viscous effects dominate over inertia, drop rolling may occur possibly even when wetting is between the Cassie-Baxter and Wenzel regimes.

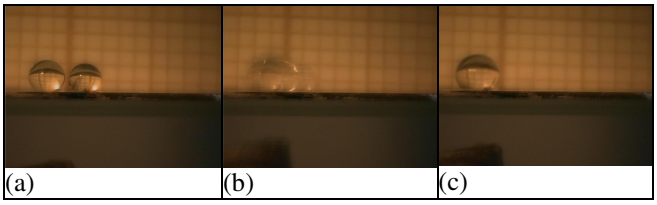

Figure 5: Coalescence of two drops on a superhydrophobic surface sample. a) A 4µl drop with paramagnetic particles on the right of the figure is displaced by a permanent magnet toward a 6µl pure water drop pinned on a surface defect. b) The two drops coalesce when they become close enough to touch. c) The combined drop from is removed from the surface defect due to the paramagnetic particles and the external magnetic field.

Coalescence of two drops was achieved by placing a 6µl water drop without particles deliberately on a surface defect to hold it. Another 4µl water drop containing paramagnetic particles was moved over the surface by the action of the magnet towards the pure water drop, until they were close enough to touch and coalesce. After coalescence, the combined drop was pulled out of the surface defect by the magnet (Figure 5). Magnetic fields can also be used to split a drop. In a drop splitting experiment, a drop was loaded with a high concentration of paramagnetic particles and two magnets were placed below the surface of the drop. The drop spread under the influence of the separating magnets until it split. From a point of view of describing the mechanism by which the paramagnetic particles act on the drop it was interesting to determine how were they distributed inside the drop while it was moving. We mounted a camera on top of the surface to record particle distribution inside a moving drop. The aggregated particle chains inside the drop were regularly distributed on the bottom of the drop as it was moving, apparently sliding with it (Figure 6).

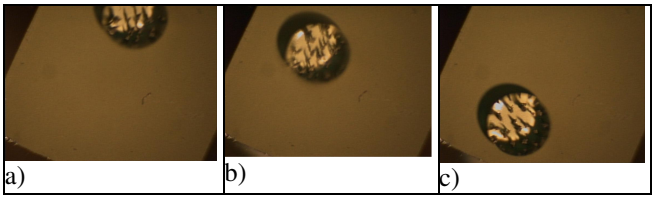

Figure 6: Distribution of paramagnetic particle aggregates inside a moving drop. Consecutive frames (a) to (c) of a moving drop taken at 10 frames per second show the relatively homogenous and stable distribution of chains sliding with the moving drop.

Our findings demonstrate the feasibility of using magnetic fields to move, combine and split aqueous drops on superhydrophobic surfaces at velocity on the order of 7cm/sec. The maximum attainable speed remains to be determined, since the maximum speed in this experiment was limited by the maximum magnet speed. This speed might be higher by achieving higher magnet speeds. This methodology appears a promising way to manipulate small discrete amounts of water.

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