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Barcelona, Catalonia (SPAIN)
16 - 20 June 2013

PARALLEL ORAL SESSIONS

Flexible Technology	Microfluidics	Composite Materials & Characterization	Optical and Fluidic Systems
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Session Chairs:			
X. Wang, *Tsinghua University, CHINA*	Y.-C. Lin, *National Cheng Kung University, TAWAIN*	C. Nguyen, *University of California, Berkeley, USA*	K. Böhringer, *University of Washington, USA*
L. Sarro, *Delft University of Technology, THE NETHERLANDS*	R. Zengerle, *University of Freiburg - IMTEK, GERMANY*	S. Tatic-Lucic, *Lehigh University, USA*	T. Cui, *University of Minnesota, USA*
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HYDROCHLORIC ACID-IMPREGNATED PAPER FOR LIQUID METAL MICROFLUIDICS

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ABSTRACT

We report a method of substantially improving lyophobicity of a paper against gallium-based liquid, using hydrochloric acid (HCl) impregnation. We also report an extremely simple fabrication of microfluidic channels on a HCl-impregnated paper for gallium-based liquid metal, Galinstan®. Paper has many favorable properties in microfluidic applications, such as low cost, abundant supply, easy fabrication, and flexibility. We evaluated lyophobicity of several papers by measuring static and dynamic contact angles with a goal of finding optimal super-lyophobic paper-based substrate for microfluidics applications. We found HCl-impregnated laser printer flattened paper towel shows appropriate super-lyophobicity. We performed a bouncing experiment of a Galinstan® droplet on the HCl-impregnated flattened paper substrate and demonstrated movement of a liquid metal droplet in microfluidic channels formed on the HCl-impregnated paper.

KEYWORDS

HCl, paper, microfluidics, lyophobicity, Galinstan®

INTRODUCTION

Paper is inexpensive, abundant, easy to handle, and flexible material. It is well known for its super-hydrophilic characteristics and the water contact angle is known to be in the range of 0º ~ 26º [1]. Recently, there have been interesting studies to use modified papers as microfluidic platforms. Martinez *et al.* reported photoresist impregnated paper as microfluidics channels and demonstrated the microfluidic paper-based analytical devices [2]. Chitnis *et al.* reported a method of converting paper's hydrophilicity into hydrophobicity using a CO_2 laser [3]. Although it is in its infancy, study on paper-based microfluidics is very appealing because it has potential to realize extremely low cost disposable lab-on-a-chip devices on papers.

Gallium-based liquid metals such as EGaIn (a binary alloy) [4] and Galinstan® (a ternary alloy) [5] have been increasingly studied as an alternative to mercury due to its non-toxic nature. However, they are readily oxidized in air and form a thin oxide layer causing the alloy to adhere to almost any surface [6]. It was reported that HCl solution can remove the oxide skin from gallium-based liquid metal [7]. Recently, we demonstrated a method of using HCl vapor to remove the oxide layer on the surface of the alloy resulting in the recovery of nonwetting characteristics [8].

In this paper, we studied variously treated papers by measuring static and dynamic contact angles, and carried out an encapsulation and bouncing experiment of the Galinstan® droplet on a HCl-impregnated flattened paper. We also report an extremely simple method of fabrication of microfluidic channels on a HCl-impregnated paper and demonstrated manipulation of liquid metal on it.

EXPERIMENT

Materials

In this work, we purchased Galinstan® from Geratherm Medical AG and used it without any modification. The composition rate of the Galinstan® is 68.5% gallium, 21.5% indium, and 10% tin.

The paper used in this work was a conventional paper towel (Uline S-7127) as seen in daily life. Figure 1 shows scanning electron microscopy (SEM) and optical images of a paper clearly showing millimeter-sized bumpy surface patterns and hierarchical micro/nano sized randomly distributed cellulose fibers resulting in high porosity. As it is well-known, such a paper is extremely hydrophilic due to the high porosity.

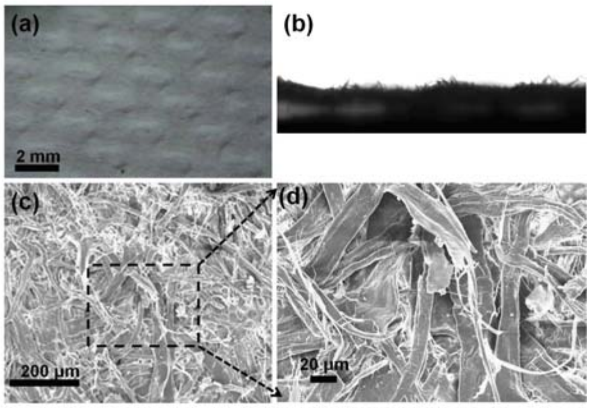

Figure 1: Optical and SEM images of a paper (a) top-view, (b) side-view, (c) and (d) close-up view showing highly porous, randomly oriented hierarchical micro/nano cellulose fiber structures.

Static/Dynamic Contact Angle Measurement

We tested the paper for its lyophobicity by measuring static and dynamic contact angles of the Galinstan®. In order to increase the lyophobicity of the paper, we treated the paper with three different methods and their combinations: flattening the paper by running through a laser printer fuser, fluorocarbon (FC) polymer coating (~20 nm), and HCl (37 wt%, 7μL) impregnation. From the combinations of three methods above, five different types of paper were made and tested: a non-treated paper; a flattened paper; a FC coated paper; a FC coated flattened paper; a HCl-impregnated flattened paper.

For static contact angle measurement, we deposited ~7.8 μL Galinstan® droplets on the papers with various treatments using a pipette, and measured the static contact angles using a goniometer (Ramé-Hart 260-F4). For dynamic contact angle measurement, we kept adding and removing the volume of Galinstan® on the diversely modified papers using a pipette with Teflon®-coated tip (inner diameter of 0.3 mm) while the side view of the droplet was recorded by a charge-coupled device (CCD) camera at 70 frames per second. The advancing and receding contact angles were obtained from the frame of the recorded movie just before contact line moved. The maximum and minimum angles was used as advancing angle and receding angle, and the difference between the advancing angle and the receding angle (contact angle hysteresis) was used to determine the sliding angle of a liquid droplet.

In these measurements, the static and dynamic contact angles can significantly denote the wetting characteristic of the Galinstan® droplet on the papers with various treatments. A humidity of 46.9 ± 0.8% and a temperature of 22.9 ± 0.2 °C was the condition for measuring the static/dynamic contact angle.

RESULTS AND DISCUSSION

Static/Dynamic Contact Angle

Figure 2 shows Galinstan® droplet's static contact angles on the papers with various treatments. The measured static contact angle of the paper with no treatment was 142.8 ± 5.7º which is substantially higher than that of the FC polymer-coated plane polydimethylsiloxane (PDMS). This shows that paper itself has lyophobicity against Galinstan®. The papers treated by flattening (150.3 ± 1.8º), by FC polymer coating (146.5 ± 2.8º) and by flattening and FC polymer coating (152.3 ± 6.5º) show further increase of the static contact angles. However, the shapes of Galinstan® droplets on those surfaces are irregular because the Galinstan® immediately oxidizes in air environment and thus it has viscoelastic characteristic as shown in Figure 2. Interestingly, the contact image of the Galinstan® droplet on the HCl-impregnated flattened paper shows the shape of a simple sphere and displays the static contact angle of 149.9 ± 0.6º. The contact angle of the HCl-impregnated flattened paper is not the highest, but the HCl-impregnated flattened paper shows the most consistent contact angles during repeated experiments.

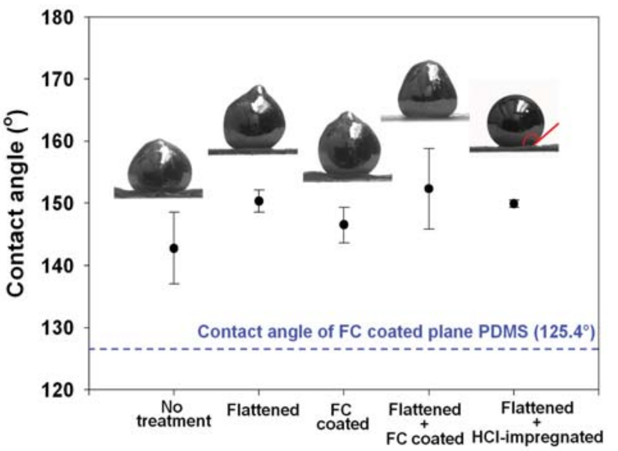

Figure 2: Static contact angles of ~7.8 µL Galinstan® droplets on papers with various treatments.

Figure 3a shows the dynamic contact angles of Galinstan® on the papers with various treatments. Red-colored circle dot shows advancing contact angles and blue-colored square dot shows receding contact angles, respectively. The advancing contact angles of all papers are very close to or higher than 150º. However, the receding contact angle greatly depends on the treatment. The non-treated paper shows the lowest receding contact angle of 97.5º, while the HCl-impregnated flattened paper shows the highest receding contact angle of 139 º as shown in the inset images of Figure 3a. As a result, the contact angle hysteresis for the paper with various treatments is shown in Figure 3b. The paper without any treatment showed the contact angle hysteresis of 52.5º. The FC coated paper showed contact angle hysteresis of 27.2º, which shows more lyophobicity than the paper with no treatment. The HCl-impregnated flattened paper showed substantially improved lyophobicity, showing the contact angle hysteresis of only 11º.

Based on the static and dynamic contact angle study, the HCl-impregnated flattened paper displayed consistent static contact angles and the lowest contact angle hysteresis for the Galinstan®. The reason is that the oxidized Galinstan® chemically reacts with HCl on the paper, resulting in surface change of the liquid metal [8].

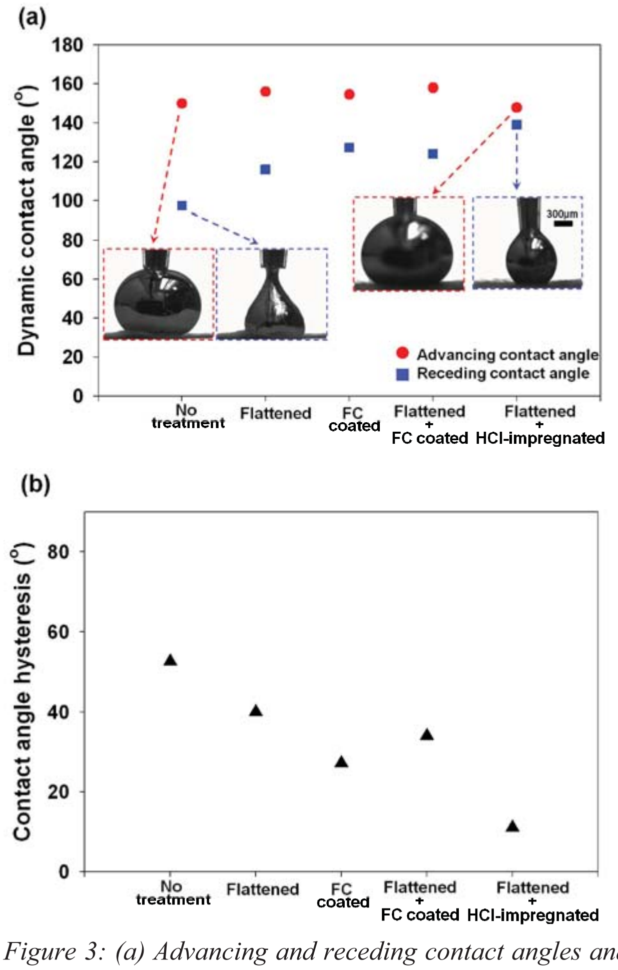

Figure 3: (a) Advancing and receding contact angles and (b) contact angle hysteresis for papers with various treatments. Inset images in (a) show images of advancing and receding of Galinstan® on the non-treated paper and the HCl-impregnated flattened paper.

Bouncing Experiment

The measured static contact and dynamic angles of the Galinstan® droplet on the various papers represent a great potential of the HCl-impregnated flattened paper as a non-wetting substrate for Galinstan® microfluidics. To further verify the lyophobicity of the surface, we carried out bouncing experiments of a Galinstan® droplet (~7.8 µL) on the flattened paper and the HCl-impregnated flattened paper. In this experiment, each droplet impacted the substrates while the movement of the droplet was being captured by using a high-speed camera (Photron SA4) with 1000 frames per second.

Figure 4 shows a series of images of Galinstan® droplet falling from 3 cm above the surface of a flattened paper and a HCl-impregnated flattened paper, respectively.

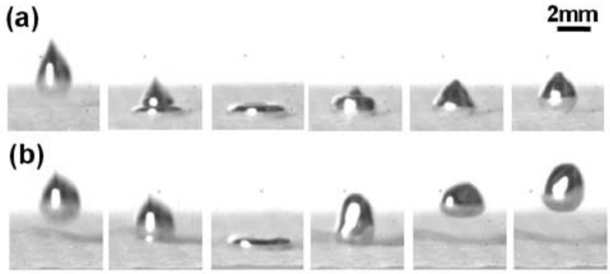

Figure 4: A series of time-lapse images of a Galinstan® droplet falling from 3 cm above the surface on (a) a flatten paper and (b) the HCl-impregnated flattened paper.

The shape of oxidized Galinstan® droplets in each bouncing experiment (Figure 4a and 4b) was not spherical before hitting the paper because the droplet had been exposed to air and thus the oxide layer covered the surface of the droplet. After the droplet hit the surface, it spread on the surface and never bounced back on the flattened paper (Figure 4a), while the droplet readily bounced off from the surface of the HCl-impregnated flattened paper without leaving any residue on the substrate (Figure 4b). These results clearly prove that the adhesion of Galinstan® droplet on the HCl-impregnated paper is negligible.

Encapsulation Experiment

Since HCl solution can evaporate in ambient environment, we placed a ~7.8 µL Galinstan® droplet in a quartz container to prevent complete evaporation of HCl from the paper substrate. We investigated the reliability of the encapsulation by measuring the contact angle of the Galinstan® droplet on the HCl-impregnated flattened paper as a function of time using a goniometer.

Figure 5a shows the contact angle change of the Galinstan® droplet on the HCl-impregnated flattened paper encapsulated in the quartz container (Figure 5b).

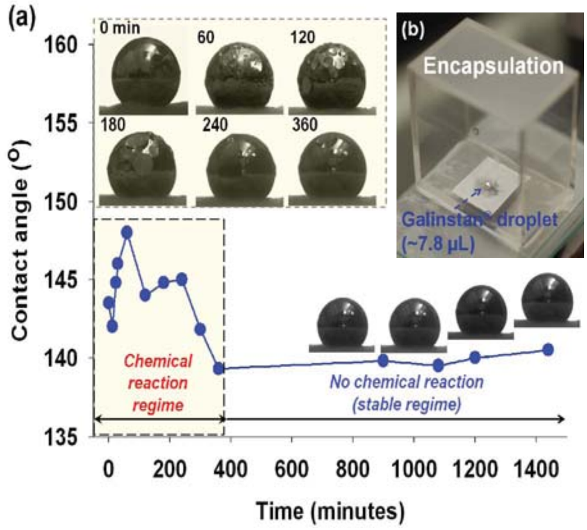

Figure 5: (a) Contact angle change of the Galinstan® droplet on a HCl-impregnated flattened paper. (b) An encapsulation container was used to prevent evaporation of HCl.

We measured the static contact angles of the Galinstan® droplet on the HCl-impregnated flattened paper until 24 hours right after the encapsulation. Galinstan® droplet reacts with HCl from the paper for the first 6 hours and the contact angle varies within limited range. However, after 6 hours, the contact angle does not drastically change over a long period of time maintaining super-lyophobicity.

This measurement confirms that Galinstan® droplet on the HCl-impregnated paper can react with HCl from the paper for certain time and afterward becomes stable to sustain the lyophobic characteristic by encapsulation.

Microfluidic Channel Fabrication

Based on the measured static and dynamic contact angles, in conjunction with the results from the bouncing and encapsulation experiments, we concluded that the HCl-impregnated flattened paper can be used as a super-lyophobic microfluidic substrate for the oxidized Galinstan®.

We then studied a method of extremely simple fabrication of HCl-impregnated paper-based microfluidic channels. The fabrication process is illustrated in Figure 6a. The grid-shape 1/16 inch (1.57 mm) diameter stainless rods were placed on the paper, which in turn was placed on a deformable material. Pressure was applied through a top plate (blue-colored in the figure), micro imprinted grid of microfluidic channels with channel depth of approximately 1.2 mm was created on the paper. The oxidized Galinstan® droplet was then placed by a pipette (Figure 6b), and mobilized by pressurized N_2. Figure 6c shows a series of still images from a real-time video of a moving oxidized Galinstan® droplet on the HCl-impregnated flattened paper. The speed of the Galinstan® droplet on the HCl-impregnated flattened paper was measured to be approximately 2.5 cm/sec. It should be noted that there is no trace of oxidized Galinstan® on the HCl-impregnated flattened paper, clearly showing this paper-based substrate is suitable for Galinstan®-based microfluidic applications.

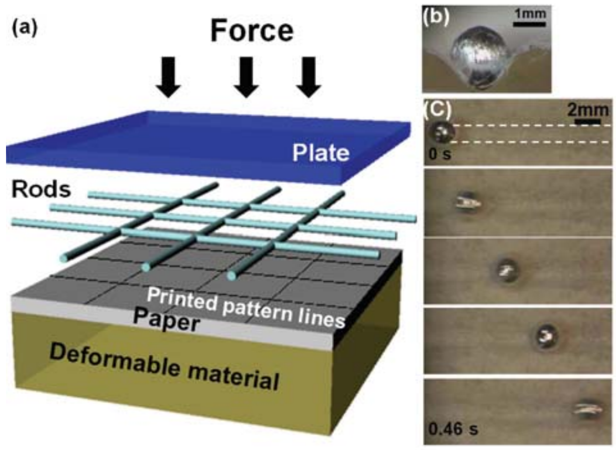

Figure 6: (a) Schematic of paper-based microfluidic channel fabrication using a deformable substrate, (b) optical image of 7.8 μL Galinstan® droplet placed on the paper microfluidic channel, and (c) a series of still images taken from a real-time video of a moving Galinstan® droplet on a HCl-impregnated flattened paper.

CONCLUSION

In this paper, variously treated papers were tested for their lyophobicity against Galinstan® by measuring static and dynamic contact angles. The HCl-impregnated flattened paper turned out to be a super-lyophobic substrate, displaying a very large static contact angle (149.9 ± 0.6º) and a small contact angle hysteresis (11º). As a further demonstration of super-lyophobicity of the treated paper, we performed a bouncing experiment and encapsulation experiment to show the feasibility of the paper as a microfluidic platform for gallium-based liquid metal. As a final step, super-lyophobic microfluidic channel structure based on a HCl-impregnated flattened paper was presented as a suitable microfluidic platform for the manipulation of oxidized Galinstan® droplets. We believe that this work has a great potential to solve one of the most challenging obstacles in the liquid metal based microfluidics.

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