Sensors and Actuators B 207 (2015) 199–205

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Hydrochloric acid-impregnated paper for gallium-based liquid metal microfluidics

Daeyoung Kim [a,b,*], Yunho Lee [c], Dong-Weon Lee [d], Wonjae Choi [c], Koangki Yoo [e], Jeong-Bong (JB) Lee [a]

[a] Department of Electrical Engineering, The University of Texas, Dallas, TX, USA
[b] Department of Electrical Engineering, Korea Army Academy, Yeong-Cheon, South Korea
[c] Department of Mechanical Engineering, The University of Texas, Dallas, TX, USA
[d] School of Mechanical Systems Engineering, Chonnam National University, Gwangju, South Korea
[e] Department of Information and Communication Engineering, Hanbat National University, Daejeon, South Korea

ARTICLE INFO

Article history:
Received 2 May 2014
Received in revised form
13 September 2014
Accepted 29 September 2014

Keywords:
Liquid metal
Galinstan®
HCl-impregnation
Super-lyophobicity
Microfluidic platform

ABSTRACT

We report a simple hydrochloric acid (HCl) impregnation method to substantially improve the lyophobicity of a paper against gallium-based liquid metal. Based on the HCl-impregnated paper, we also propose an extremely simple fabrication method of microfluidic channel for gallium-based liquid metal, Galinstan®. Due to its low cost, easy fabrication, and flexibility, recently paper has drawn attention as microfluidic platforms for various applications. We have treated two different types of paper (paper towel and printing paper) with various treatment methods such as laser printer flattening, fluorocarbon polymer coating, HCl-impregnation, and combination of these methods. We then studied their lyophobicity characteristics by measuring static and dynamic contact angles as well as bouncing experiment. We found that HCl-impregnation is a simple yet powerful method to engineer certain types of papers to make them super-lyophobic substrates against gallium-based liquid metals and effective for more than 30-days after impregnation. To show the feasibility, we demonstrated manipulation of a Galinstan® droplet along microfluidic channels formed on the HCl-impregnated paper.

1. Introduction

Paper is abundant and extremely cheap cellulosic material. Untreated paper is highly porous and thus paper can easily absorb most liquids. Due to these properties, paper can transport fluid only using capillary force without any active pumping system [1]. Great potential of paper as disposable microfluidic platforms has only recently unleashed and there have been demonstrations on the paper-based microfluidics for analytical chemistry [2], health diagnostics [3,4], and environmental monitoring [5] for the past few years. In these work, microfluidic channels were typically fabricated by patterning hydrophobic regions on super-hydrophilic papers. Chitnis et al. reported a method of converting paper's hydrophilicity into hydrophobicity using a CO_2 laser [6]. Balu et al. demonstrated that super-hydrophobicity can be created on a paper surface via a combination of etching by an oxygen plasma and deposition of a fluorocarbon film [7]. In addition, Bruzewicz et al. used polydimethylsiloxane (PDMS) to define hydrophobic microfluidic channels in a paper [8]. Based on these ease fabrication merit of paper-based microfluidic devices, various researches use expensive reagents as the working media [9,10] because paper offers a wide range of other advantages, such that a paper is flexible, does not easily break, portable, liquid-wicking as received, and so forth. Therefore, although reagents or other liquids add significant amount of cost to the final product, this character of paper allows the paper-based microfluidic devices to be fabricated in countries with very poor infrastructure, and thus the paper still has a merit even if it loses its low cost benefit.

As an alternative to toxic mercury, non-toxic gallium-based liquid metal alloy such as EGaIn (a binary gallium and indium alloy) [11] and Galinstan® (a ternary alloy of gallium, indium and tin) [12] have been recently studied. Based on its favorable properties such as higher thermal and electrical conductivity compared to mercury, low melting point and low toxicity, gallium-based liquid metals have been investigated for a variety of applications including heat transfer [13], stretchable microfluidic antenna [14], hyperelastic pressure sensor [15], microfluidic wireless strain

* Corresponding author at: The University of Texas at Dallas, Department of Electrical Engineering, Richardson, United States. Tel.: +1 9726930988.
E-mail address: jokuksarang64@gmail.com (D. Kim).

http://dx.doi.org/10.1016/j.snb.2014.09.108
0925-4005/

sensor [16] and tunable frequency selective surface [17]. However, gallium is readily oxidized in air, forming a gallium oxide layer at the outer skin of the gallium-based liquid metal alloys. This causes the gallium-based liquid metals to be viscoelastic and to adhere to almost any surface [18], which is an extremely challeging ptoblem to solve.

In microfluidic devices such as a stretchable microfluidic antenna, a hyperelastic pressure sensor, and a strain sensor, liquid metal fills the entire microfluidic channel and the oxide layer does not compromise the performance of the device rather enhances the adhesion between the liquid metal and the surface of channel. However, for applications such as heat transfer and a microfluidics-based switch in which it is essential to have a dynamic movement of the meniscus of liquid metal, the viscoelastic oxide layer is severely problematic. There have been several efforts to overcome this issue by using non-wettable surface against oxidized gallium-based liquid metal. It was reported that HCl solution or vapor can chemically remove the oxide skin from gallium-based liquid metal [19–21]. Rather than removing oxide skin, it was also reported that hierarchical micro-/nano-scale structured surface is super-lyophobic and oxidized Galinstan® does not adhere to the engineered surface [22].

In this paper, we report lyophobicity of (i) a paper towel and a printing paper, (ii) papers treated with laser printer flattening, fluorocarbon polymer coating, and HCl-impregnation, as well as their combinations. We characterized the lyophobicity by measuring static and dynamic contact angles and observing bouncing patterns of naturally oxidized Galinstan® droplets on various paper-based substrates. In addition, we demonstrated Galinstan® droplet manipulation on a HCl-impregnated paper as a substrate.

2. Method of experiment

2.1. Materials

In our study, we chose two different papers: a conventional paper towel (Uline S-7127, Uline, Pleasant Prairie, WI, USA) and a printing paper (Office Depot #348037, letter-sized, Boca Raton, FL, USA) which are widely used in our daily life. Conventional paper towel is extremely hydrophilic, and readily absorbs water due to its chemical preference and porous structure; its cellulose which has hydroxyl group prefers to have hydrogen bonding with water molecules and its cellulous fibers formed spatial solid network at the paper making process. The printing paper used in this experiment was for the inkjet printing, and thus, the surface of the paper was extremely smooth and easily absorbs water-based ink. However, if the printing paper has super-hydrophilicity, the water can spread to nearby regions and distort the printed image. Therefore, it was chemically treated with starch to have some degree of hydrophobicity [23,24]. In addition, calcium carbonate and titanium dioxide were deposited to modify the brightness and optical property of the paper [25,26].

Fig. 1 shows top-view scanning electron microscopy (SEM) images of a conventional paper towel and a printing paper. Both papers show micro-/nano-scale randomly distributed cellulose fibers. As shown in the SEM images, the porosity of the paper towel is larger than that of the printing paper as the surface of the printing paper was chemically treated with starch, calcium carbonate, and titanium dioxide (Fig. 1d). Numerically, we calculated density of the papers used in this experiment based on the given information from the company. They were turned out to be 0.150 g/cm^3 for the paper towel and 0.735 g/cm^3 for the printing paper.

2.2. Static/dynamic contact angle measurement

We investigated wetting characteristics of papers against naturally oxidized Galinstan® by measuring static and dynamic contact angles. In order to increase the lyophobicity of two papers, we modified the paper with three different methods and their combinations: flattening the paper towel by running through a laser printer fuser, fluorocarbon (FC) polymer coating (~20 nm) by applying inductively coupled plasma power with a mixture of fluorocarbon precursors (C_4F_8) and Ar gas, and HCl (37 wt%, 7 μL) impregnation. From the combinations of three methods above, eight different types of paper were made and tested: non-treated paper towel

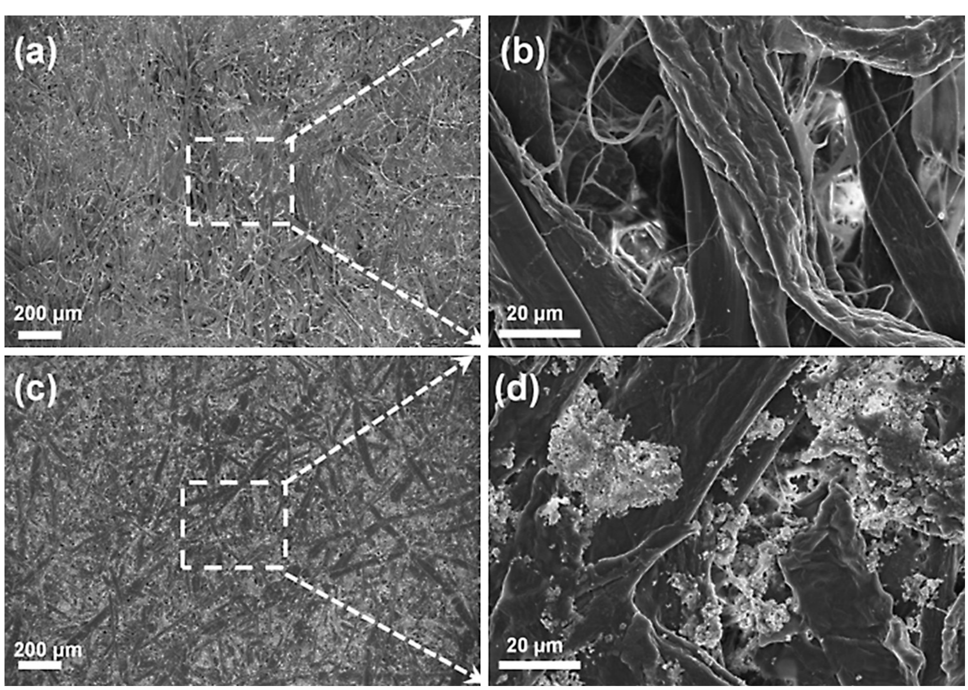

Fig. 1. SEM images of (a and b) a paper towel and (c and d) a printing paper; (b) is close-up view of (a) showing highly porous, randomly oriented micro-/nano-scale cellulose fiber structures; (d) is close-up view of (c) showing chemical treatment.