A LOW-VOLTAGE MICROFLUIDIC VALVE BASED UPON A REVERSIBLE HYDROPHOBICITY EFFECT

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ABSTRACT

We report a microfluidic valve based on a reversible hydrophobicity effect via the growth and retraction of non-volatile nano-textured dendritic silver filaments on the surface of a solid electrolyte. A 6 V DC bias grows or dissolves, depending on the polarity, filaments which are tens to hundreds of nanometers in height. The valving function of these nano-filaments, which occurs within approximately 25 sec, was demonstrated by monitoring the fluid flow in a 250 μm wide, 25 μm deep PDMS-enclosed channel.

INTRODUCTION

Valves in microfluidics control routing, timing and separation of fluids [1]. Most currently employed valves are made of PDMS and their operation relies on the deformation of thin film or bulk PDMS to obstruct or permit fluid flow [2-6]. However, such techniques, in general, require large mechanical structures, complicated integration into

microfluidic channels and cumbersome external pneumatic accessories [7-12].

We report a unique mechanism to control the fluid flow - the growth or retraction of nano-scale dendritic metallic filaments (Figure 1a&b). The nano-filaments manipulate hydrophobicity and contact angle hysteresis on the interface between the fluid and the channel surface [13], rather than the bulk of the flow, to provide flow regulation. Microfluidic channels are typically 10s or 100s of μm in depth, while our valve operates on a scale of 10s to 100s of nm (Figure 1c&d). This nano-structure changes the critical dynamic characteristics on the bottom surface of the channel, emulating the transition from the lotus effect to the petal effect. The petal effect was found to be based upon hierarchical micro- and nano-structures which significantly contribute to the adhesive force on a fluid droplet [14,15]. The nano-scale dendritic filaments enhance the roughness to interrupt flow [16,17] and modulate the interface topography on the bottom of a PDMS-enclosed microfluidic channel (Figure 1e).

Figure 1: Electrodeposition of metallic nano-filaments on the surface of a solid electrolyte. **a.** Schematic of the growth of dendritic silver nano-filaments on a chalcogenide solid electrolyte surface. **b.** The growth and retraction processes of nano-filaments depending on the polarity of 6 V DC bias. **c.** Filament morphology taken by scanning electron microscope (SEM), showing maximum of 200 nm height of nano-filaments. **d.** Optical profilometer image illustrating filament morphology. **e.** The cross-sectional view of the valve.

The bulk flow is pinned by the adhesive force from the channel bottom where the liquid-solid interface forms, which clearly differentiates our approach from existing work that incorporates the liquid-air interface of the droplet exposed to the air. In the case of microfluidic flow, the attractive force between liquid molecules and the cohesive force between solid surface and liquid molecules dominate the flow characteristics [18]. When the fluid molecules adjacent to the channel bottom are stopped, the molecules inside the bulk microfluidic also stop accordingly due to the attractive intermolecular force [19]. From the macroscopic viewpoint, the dynamic viscosity of microfluidic flow is extremely high, which impedes sliding between adjacent laminar flow layers occurring at significantly low Reynolds number [20,21]. This is a unique property of low Reynolds number microfluidic flow which does not occur in macro-scale fluidic settings as the viscous force fails to hinder the movement of the bulk in these.

Instead of the cumbersome pneumatic elements and air tubing, the nano-scale valve is actuated by a low DC bias ($\leq 6V$), allowing the external unit to be a simplified standard DC power supply. Unlike the pneumatically actuated devices, where the air may penetrate through the thin PDMS membrane and dissolve into the biological / chemical samples in the channel, the nano-scale valve is free from such contamination.

RESULTS

A constant DC supply, rather than a pulse modulated voltage, was found to be preferential to facilitate rapid and directional nano-filament growth, (Figure 2a). In both 50% and 80% duty cycle pulse-width-modulated (PWM) supplies, multiple nucleation sites were observed during the growth process. These sites initiated the nano-filaments independently and formed rather randomly dispersed growth of nano-filaments from the cathode tip. Figure 2b shows the exponential dependence of the growth rate on applied DC voltage ($\leq 6V$), matching well with simulated values. The simulation is based on an electrodeposition model which couples electrochemical theory with a random walk/diffusion component to multiple incidences of dendrite growth for each condition [22]. At 6V DC, the growth rate became 18-20 $\mu\text{m}/\text{sec}$, thus the nano-filaments grow from the cathode and reach the anode within 12-14 seconds for a 250 μm wide channel.

Figure 2: Control of nano-filaments growth. **a.** Filaments generated by DC bias and pulse width modulation (PWM) with different duty cycles. **b.** Filament growth rate as a function of applied DC voltage.

The petal effect requires two attributes: i) hydrophobic surface with contact angle (CA) $> 90^\circ$, and ii) high contact angle hysteresis (CAH) responsible for high adhesive force (Table 1). Three hydrophobic materials, including rough Ag, smooth Ag, and parylene, and two hydrophilic materials, including chalcogenide glass (Ge-Se) and SiO_2 , were evaluated for CA and CAH. Note that the measured CA of rough and smooth silver showed little difference, yet the CAH measurements gave significantly different results: 74° for rough Ag vs. 54° for smooth Ag. Figure 3a illustrates the roughness, R_f , incurred by the nano-filaments, which promote high CA and CAH of hydrophobic (solid lines) surfaces, yet lower the CA and moderately improve the CAH of hydrophilic (dotted lines) surface. The silver nano-filaments were covered by a thin parylene film, 200 nm thick, to prevent direct contact to the bio-sample in the channel to avoid silver contamination (Figure 3b), and their nano-scale rough topography was projected through the parylene layer to generate significant roughness features above the parylene surface (Figure 3c). If either CA or CAH requirement is unmet, the valve will not work. For instance, a valve with a SiO_2 patch showed the roughness of protruding filaments but failed to stop the flow because SiO_2 is hydrophilic.

Table 1. Measured contact angle (CA) and contact angle hysteresis (CAH) of different materials using a Rame-Hart Goniometer.

Materials	CA [Deg] $\pm$ s.d.	Advancing angle [Deg] $\pm$ s.d.	Receding angle [Deg] $\pm$ s.d.	CAH [Deg] $\pm$ s.d.	$\cos\theta_{\text{rec}} - \cos\theta_{\text{adv}}$
Rough silver	94 $\pm$ 1	98 $\pm$ 2	24 $\pm$ 2	74 $\pm$ 3	1.05
Smooth silver	93 $\pm$ 1	114 $\pm$ 2	60 $\pm$ 2	54 $\pm$ 3	0.91
Parylene	87 $\pm$ 1	97 $\pm$ 2	64 $\pm$ 2	33 $\pm$ 3	0.56
Chalcogenide	69 $\pm$ 1	46 $\pm$ 1	22 $\pm$ 1	24 $\pm$ 1	0.23
Silicon dioxide	44 $\pm$ 1	39 $\pm$ 1	25 $\pm$ 1	14 $\pm$ 1	0.13

Figure 3: Characterization of the nano-filaments. **a.** Contact angle (CA) and contact angle hysteresis (CAH) as a function of roughness, R_f , of a hydrophobic silver surface (solid line) and a hydrophilic SiO_2 surface (dashed line). **b.** The visualization of nano-filaments under a 200 nm thick parylene, showing the nano-filaments grow underneath the parylene film (contrast). **c.** The topography profiles of the surfaces of parylene, silicon dioxide and chalcogenide solid electrolyte, from the top down, using a stylus profilometer.

Figure 4a shows the setup to evaluate the effectiveness of the nano-valve in a 25 μm deep PDMS-enclosed microfluidic channel. The fluid flow could be stopped and restarted by nano-filaments within ~ 25 seconds of actuation (Figure 4b). The nano-filaments are persistent and therefore no static power is required to retain the on/off states of the valve. We attempted valving in channels up to 30 μm deep and up to 250 μm wide, which were all successfully regulated by the nano-valve. However, the nano-filaments failed to regulate the flow in 50 μm deep channel. This is likely due to the lack of a sufficiently strong hydrophobicity control of such a large fluid bulk, especially in the liquid located far from the nano-filament surface. The nano-valve was evaluated by flow rate measurements and visualized by suspended microspheres in the fluid (Figure 4c). The number of microspheres in individual regions was counted in different phases (Figure 4d), corresponding to the phases shown in Figure 4b. Region 1 had fewer and slower microspheres than region 4 when the valve was in the process of opening and closing. The trend was also apparent in the period of reopening the channel. This trend matched the presence of partial nano-filaments. The region where the nano-filaments existed had fewer and slower microspheres than the region where the nano-filaments retracted or did not yet reach. The behaviors of the microspheres reflected the flow rate of the liquid flow, thus this observation was consistent with the filament growth-induced hydrodynamic changes.

Figure 4: Testing of valves in standard PDMS-based microfluidic channels. **a.** Experimental setup for the nano-valve in a microfluidic channel. **b.** On/off valve operation: bias (red) and the corresponding measured flow rate (blue). **c.** The visualization of the microfluidic flow via monitoring of 5 μm diameter microspheres inside the liquid. **d.** Counts of microspheres in the individual regions at different windows of time corresponding to the phases shown in (b).

The nano-valve has much room to improve. The current growth / retraction rates are relatively low so that actuation time constants are in the order of 10s of seconds for a 250 μm wide channel. The growth / retraction rates can be improved by optimizing the chalcogenide materials and by moving to higher bias. The electrodes shape was tapered to focus the electric field at the tip, however, multiple growth / retraction sites often became activated at the tip and the tapered sides of the electrode. One may passivate the tapered sides of the electrode by covering the electrode, except the tip, using an inert material, to allow electric field focusing at the tip to grow nano-filaments only at the tip.

The nano-valve benefits from a unique operating mechanism, deploying nano-scale rough solid to liquid interfaces, requires no pneumatic accessories to operate, and thereby may offer attractive potential in micro-/nano-fluidics. Unlike existing pneumatic valves, the nano-valve demands no static power consumption to retain the on/off states of the valve. This feature becomes critical when a large array of valves needs to be integrated in a power-critical setting, such as microfluidic portable analyzers. The nano-valve is scalable. When the feature sizes are scaled down to form a nano-fluidic system, the nano-valve performs better. The growth / retraction rates are proportional to the electric field, thus smaller dimension increases the growth / retraction rates at a given actuation voltage.

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