Supporting Information for A Fluidic Diode, Valves and A Sequential-Loading Circuit Fabricated on Layered Paper

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1 Water contact angle measurement

Water contact angle was measured using an in-house imaging system. The system comprised a stereoscopic zoom microscope with a 45° mirror attached in front of its objective lens. Water contact angle, θ, was determined by two geometric parameters (measured in pixel unit), $\theta = 90^\circ \pm \frac{180^\circ}{\pi} \arcsin \frac{h}{r}$, where r and h were the radius of the spherical profile of the droplet and its center distance from the paper surface, respectively. The uncertainty of contact angle measurement, $\delta\theta$, was associated with the uncertainty of each individual geometric parameter, δr and δh, measured from the image. Specifically, $\delta\theta$ was calculated by the root-sum-square expression, $\delta\theta = \left[(\frac{\partial\theta}{\partial r}\delta r)^2 + (\frac{\partial\theta}{\partial h}\delta h)^2\right]^{1/2}$. In this study, δr and δh were approximately 4 pixel units. Microphotographs were recorded using the CCD camera and an illuminator (model NI-150, Nikon).

2 Patterning wettability of paper

The layered paper was patterned in a two-step reaction (Figure S1a). In the first step, cellulose fibers were primed by vinyl-terminated trichlorosilane. Condensation reaction be- tween trichlorosilane and hydroxyl groups of cellulose grafted the vinyl terminus to the fibers, which rendered the paper hydrophobic. In the next step, the vinyl terminus further reacted with a hydroxyl-terminated thiol via the click chemistry, introducing a hydrophilic group (the hydroxyl group) to the terminus. This reaction was initiated by a photoinitiator (PI), and activated by UV exposure via a photomask. The unmasked regions of the layered paper were turned hydrophilic, whereas the masked regions remained hydrophobic.

By following this scheme, we fabricated a millimeter-scale hydrophilic pattern (Figure 1b) that wicked dye-containing water (orange in color). We observed that water was absorbed quickly, and spread evenly along the pattern. The edges of the pattern were coarse. The roughness of the edges were affected by the quality of photomask, the texture of paper and the source of UV light. Lateral profile of a 5-µl water droplet on the masked, unexposed region (Inset of Figure S1b) confirmed its hydrophobic property. The water contact angle was measured as 118.3±2°. The cross section of the hydrophilic pattern (Figure S2c) showed that the UV-promoted reaction occurred both on the surface and in the body of the layered paper. This was due to the fact that the paper was turned semiopaque when soaked in organic solvents, allowing penetration of UV light. Using X-ray photoelec- tron spectroscopy, we confirmed the grafting of vinyl-terminated trichlorosilane and the hydroxyl-terminated thiol in the corresponding steps of the reaction. In addition, we ob- served that patterns reproduced from a photomask were broadened by 0.47 to 0.8 mm. Therefore, the broadening limits the resolution of the photo patterning.

The hydrophilic pattern that was used to validate the reaction scheme was imaged using a stereoscopic zoom microscope (Nikon SMZ800) attached with a CCD camera (model SPOT Insight 2MP firewire Color Mosaic, Diagnostic Instruments, Sterling Heights, MI). The fluidic diodes, the valves and the circuit were imaged using a digital single-lens reflex camera (Canon, USA).

3 Resolution of photo patterning

To characterized resolution of the photo patterning, we fabricated hydrophilic channels (wetted by dye-containing water) and hydrophobic gaps with decreasing width shown in Figure S2a and S2b, respectively. Images of the channels were scanned using a desktop scanner. The minimum reproducible widths of the channels and the gap designed on the photomask were 0.2 mm and 1.5 mm, respectively. Line width less than 0.2 mm (on the photomask) produced no channels, and a gap width less than 1.5 mm resulted in the leaking of water through the gap. Figure S2c plots the reproduced width of each channel measured as the peak-to-peak distances of the profile (plotted in the inset in Figure S2c) along the dashed line in the inset of Figure S2a. The reproduced width shifts from the designed width by 0.47 to 0.8 mm. This shift suggests that a safe distance between two channels in a photomask should be longer than 1.6 mm, which is close to the minimum width (1.5 mm) of the leaking-proof gap in Figure 2b.

4 XPS profiling

X-ray photoelectron spectra were obtained by using Perkin-Elmer 550 Multitechnique Surface Analyzer. The XPS instrument was equipped with Al Kα X-ray source (1486.6 eV)

and operated at 400W, using a pass energy of 29.35 eV. Paper samples prepared according to the two-step reaction scheme were collected after each step of the reaction, and were vacuum-dried for 24 hours before they were analyzed by XPS. Survey scans for Si 2p region and S 2p region in Figure S3 clearly indicate the grafting of allyltrichlorosilane and mercaptohexanol after the first step and the second step of the reaction, respectively.

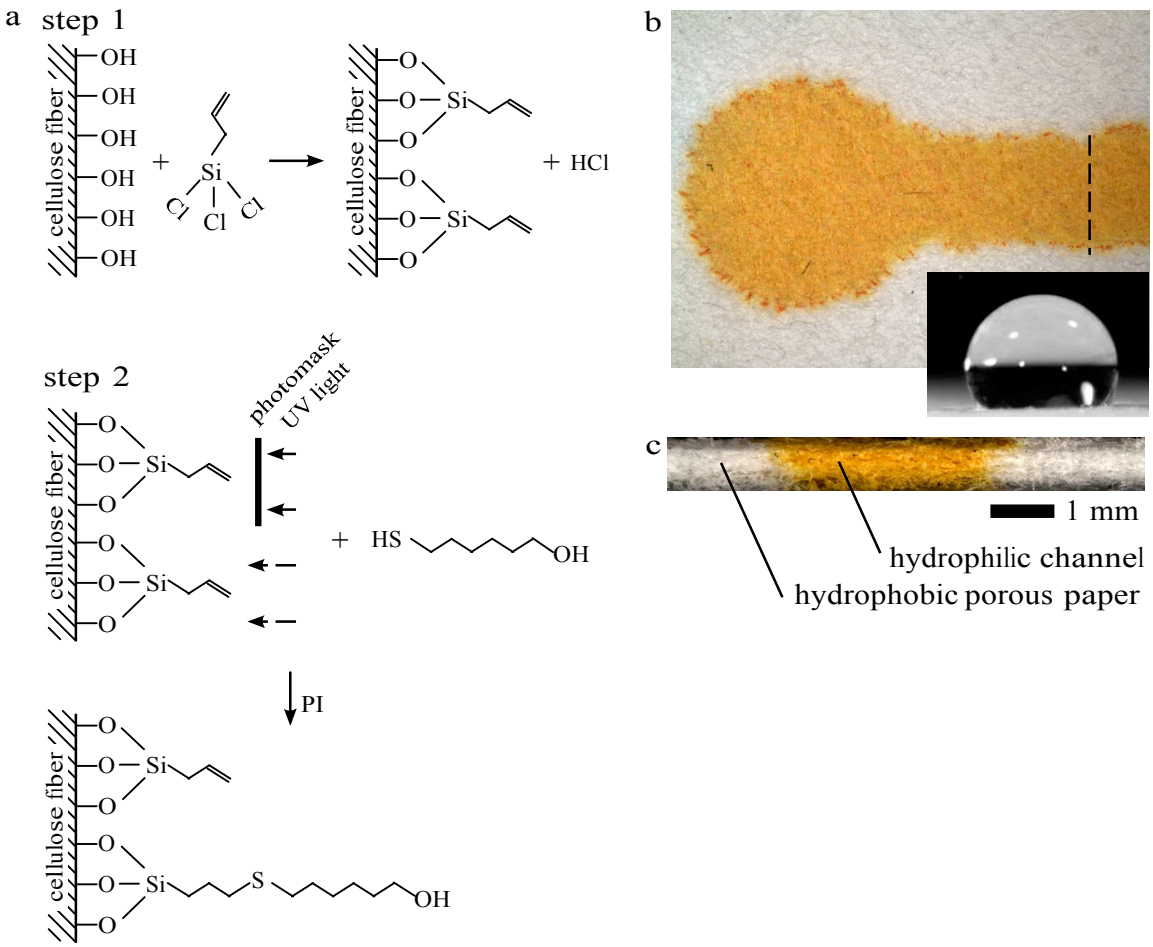

Figure S1: Photo patterning of wettability on layered paper. (a) reaction scheme. PI, photoinitiator. (b) microphotographs of a hydrophilic pattern. Inset shows the contact angle of a water droplet on the hydrophobic region. (c) view of the cross section along the dotted line in **b**.

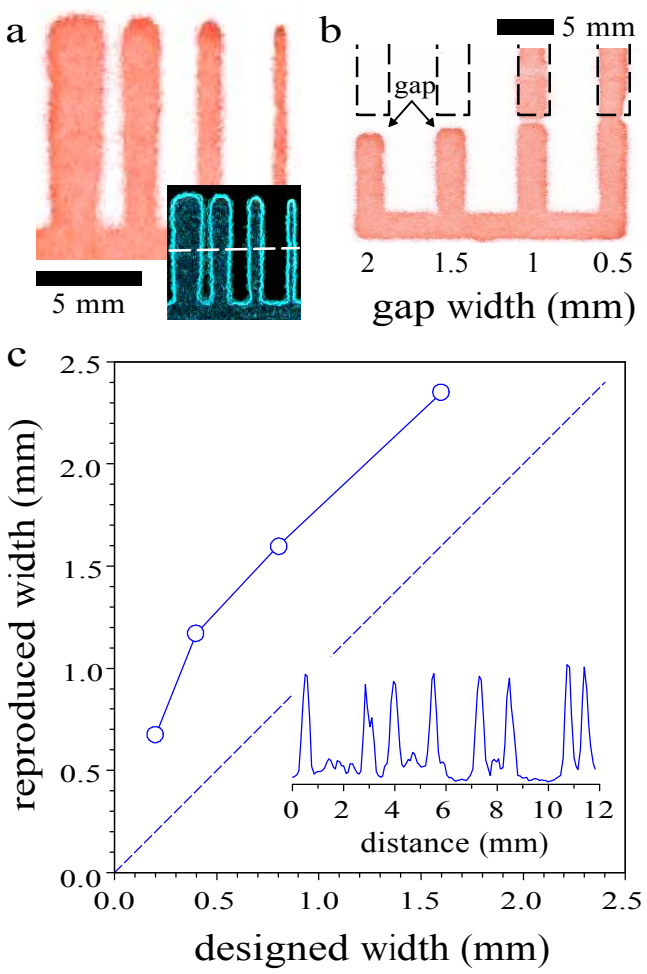

Figure S2: Resolution of the photopatterning. (a) Hydrophilic channels with decreasing width (the inset highlights the edges of the channels). (b) Hydrophobic gaps with decreasing width. The gap width refers to the width measured on the photomask. The dotted lines highlight the channels separated by the gaps. (c) Reproducibility of channel width. Inset is the intensity profile along the dashed line in (a).

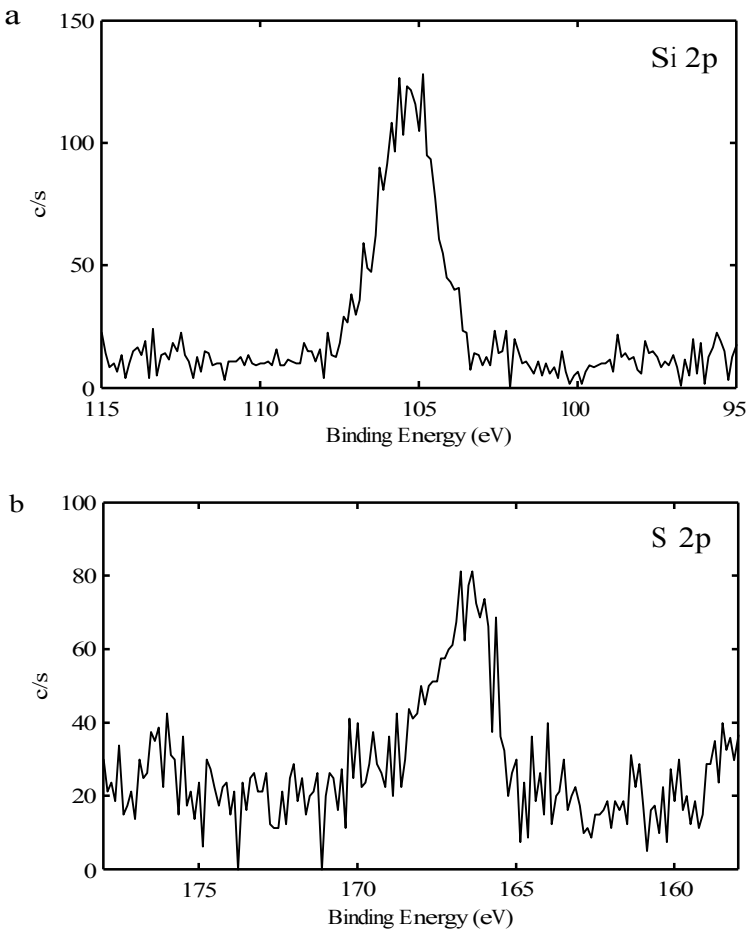

Figure S3: XPS survey scans for (a) Si 2p region and (b) S 2p region of the paper samples after the first and the second step in the reaction of photopatterning of wettability, respectively.