Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Self-driven miniaturized liquid fuel cell

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Materials and equipment

Hexadecane and dimethyl carbonate were purchased from J&K Scientific Ltd (Beijing, China). Mineral oil was obtained from Acros Organics. Span 80, sudan IV and trichlorooctadecyl silane were acquired from TCI Development Co., Ltd. (Shanghai, China). Dichloromethane, n-hexane, toluene, and ethyl acetate were purchased from Xilong Chemical Engneering Co., Ltd. (Guangdong, China). Methylene blue was obtained from Shanghai Chemical Reagent Co.,Ltd. (Shanghai, China). Four types of printing ink (cyan, black, magenta and yellow) were purchased from Mojia Consumables Co., Ltd. (Guangdong, China). Sylgard 184 PDMS oligomer and curing agent were from Dow Corning (Midland, MI). SU-8 (3035) photoresist was purchased from MicroChem.

Polytetrafluoroethylene (PTFE) tube (ID = 1.6 or 0.25 mm), PTFE three-port connector and four-port connector were purchased from Dalian Elite Analytical Instruments Co., Ltd.(Liaoning, China). The polyvinyl chloride (PVC) tube was a Tygon R-3603 tube (ID = 0.8 mm) and obtained from Guangzhou Saitop Instrument Co., Ltd (Guangdong, China). The cache chamber was fabricated in the lab.

Longer syringe pump L0107-3A was purchased from Baoding Longer Precision Pump Co., Ltd. (Hebei, China). DP 2000 digital pressure meter was obtained from Shanghai Hongyu Application Institution of Environmental Protection. (Shanghai, China). An inverted microscope (Olympus IX71) was from Olympus (Tokyo, Japan), and an Evolve 512 electron-multiplied charge-coupled device was from Photometrics (EMCCD; Tucson, USA). The photos and movies were recorded using an Iphone.

The solvent evaporation testing in PVC or PTFE tubes

To testing the solvent permeation of PVC tube, ethyl acetate solution (EA) containing 0.05% (wt) crystal violet was filled in a 10 cm PVC tube by an injector. Then, the two ends of the PVC tube was blocked by sealing plugs. We recorded the meniscus in the PVC tubes for more than one minute by an Iphone, and found that the meniscus shown a significant movement. Under the same condition, we recorded the meniscus movement in a 10 cm PVC tube with one open end.

The solvent permeation of PTFE tube was also tested by using the same method. The meniscus in PTFE tube was almost not moved, demonstrating that EA molecules cannot permeated through PTFE wall. Therefore, we used PVC tubes as evaporation tubes in the pump and the other parts of the pumps were made of PTFE.

Measurement of fluid velocity of the evaporation pump

The output tube was PTFE tube with an inner diameter (ID) of 1.6 mm. The ID of evaporation tube (EPt) was 0.8 mm. First, we fixed EPt length at 40 cm and used EA to fill the pump. After blocking the end of the EPt by a sealing plug, we observed the back flow in the output tube and recorded the time that liquid meniscus flew through a distance of 4 cm. The fluid velocity was calculated by equation (1):

$$\boldsymbol{Q} = \frac{\boldsymbol{\pi(d/2)^2 \cdot L}}{\boldsymbol{T}} \qquad (1)$$

Q was the fluid velocity, d was the ID of the output tube, L was the moving distance of meniscus, and T was the recorded time.

By using the same EPt length, n-hexane, dichloromethane, toluene, and dimethyl carbonate were used to fill the pump and measured individually. After that, we used EA as diffusing solvent, and varied EPt length at 20, 40, 60 and 80 cm. The fluid velocities in each condition were also calculated.

Pressure measurement

We used a three-port connector to construct a simple flow delivery system (Figure S1A). One port was connected to the digital pressure meter, and another port to the water vessel with a 90 cm tube. The left port was connected to the evaporation pump. After filling the pump with EA, we immediately inserted the pump into the system and measured the system pressure for 47 min with an interval of 1 min.

The environmental influence on the pumping velocities

To investigate the influence of medium, we assembled the evaporation pump with 10 cm EPt. After filling up the pump and blocking the end of EPt, we immersed the whole pump in air, DI water and 3M NaCl water solution respectively, and placed a ruler besides the output tube. Then, we took a photo of liquid meniscus every minutes in room temperature (25 ℃) by an Iphone. The moving distance of the liquid meniscus were read out from these photos.

To investigate the influence of temperature, we placed the whole evaporation pump with 10 cm EPt and the ruler into a refrigerator (-20 ℃). After 10 minutes, we started to take a photo of the liquid meniscus every minutes and dealt these photos. Under the same condition, we achieved the data of the evaporation pump with 20 cm and 40 cm EPts respectively.

To test the humidity influence, we placed the whole evaporation pump with 10 cm EPt and the ruler into a room with a relative humidity of 36 % and 66 % respectively. Then, we recorded the movement of meniscus every minute by an Iphone and read out the meniscus positions.

Microdevice fabrication

The glass substrate with Pt electrodes was purchased from Dalian Tuowei MicroChip Company. The PDMS microchannel was fabricated by standard soft microlithography process as described in elsewhere. [1] After punching through holes the PDMS slab with the channel structure and the glass substrate with Pt electrodes were played in the plasma cleaner and treated for 40 seconds. Then, the PDMS slab was bonded to the glass substrate immediately, forming the final microdevice as shown in Figure 1A. The area of single Pt electrode covered by the microchannel was 0.075 cm^2.

The evaluation of cell performance

Vanadium stock electrolyte was provided by Hunan Huifeng New Energy

Company. The V^{2+} and VO^{2+} solutions used as catholyte and anolyte, respectively, were generated from the stock electrolyte in an electrochemical cell with Pt mesh electrodes separated by a Nafion membrane. The electrolysis current is ~ 1A and the whole electrolysis process needs about 4 hours, as described in the previous work. [2]

The new generated V^{2+} and VO^{2+} solutions were degased by ultrasound for 10 minutes. Tips with 100 μL volume were inserted into the inlets and the degased V^{2+} and VO^{2+} solutions were pipetted into the tips respectively. Then, we assembled the evaporation pump with 40 cm EPt tube and connected to the outlet of the device. After the liquid flow was stable, we took the micrograph of laminar flow under an inverted microscope. Then, we connected the Pt electrodes with the electrochemical station (Solartron, SI1287/1260) and measured the polarized curve of the cell at room temperature (~ 25℃) under galvanostatic control. To changing the flow rate of the fuel cell, we varied the EPt lengths from 60 cm to 120 cm with a 20 cm interval. The polarized curves of the cell driven by the evaporation pumps with different EPt lengths were measured following the same processes.

As a comparison, we used two syringe pumps to deliver the new generated V^{2+} and VO^{2+} solutions into the inlets. The flow rates of both syringe pumps were set as 20 μL/min. After the liquid flow was stable, we measured the polarized curve of the cell at room temperature (~ 25℃) under galvanostatic control. Then, we changed the flow rates of both syringe pumps to 30 μL/min, and measured the polarized curve after forming stable laminar flow.

For LED lighting, we bonded three PDMS slabs onto the glass substrate with Pt electrodes and three fuel cells were formed in series. The evaporation pump with 120 cm EPt was divided into three outputs (O 1, O 2 and O 3) via a four-port connector (Figure S4A). Each output was connected to the outlet of a single cell respectively. The new generated V^{2+} and VO^{2+} solutions were dropped into inlets, and more than one LEDs were installed in the electric circuit. Under the suction of the evaporation pump, LEDs was lighted by the system and became dark gradually by using a clamp to stop the reactants flow.

The additional figures not displayed in the main text

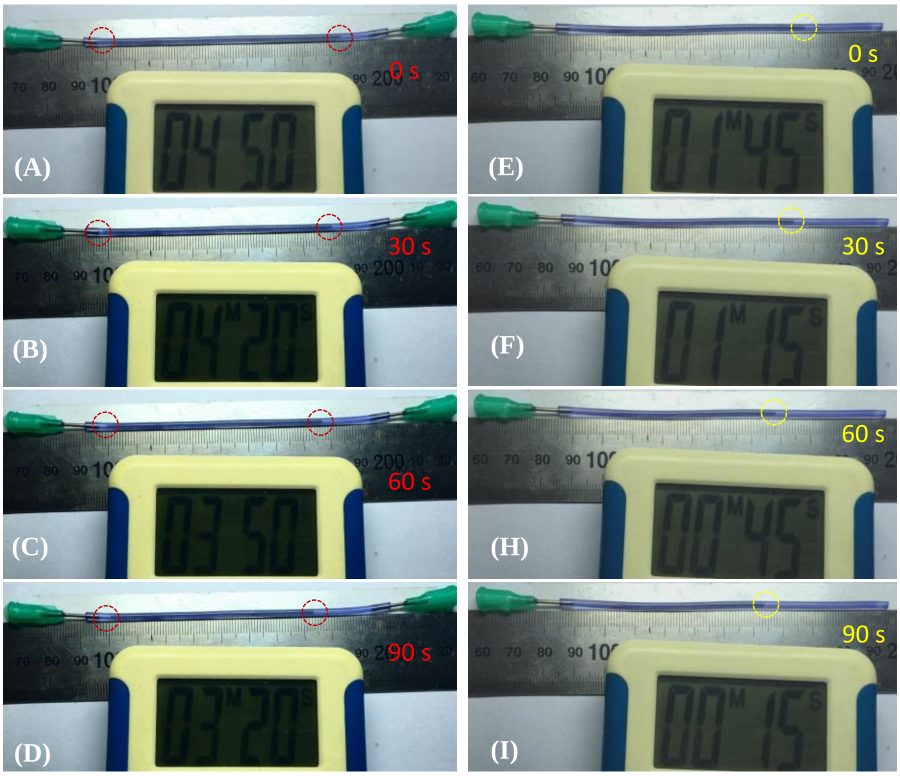


Figure S1. The solvent evaporation testing in 10 cm PVC tubes. The meniscus position in PVC tubes were recorded at an interval of 30 seconds. (A-D) are the photos of PVC tube with two blocked ends. (E-I) are the photos of PVC tube with one open end.

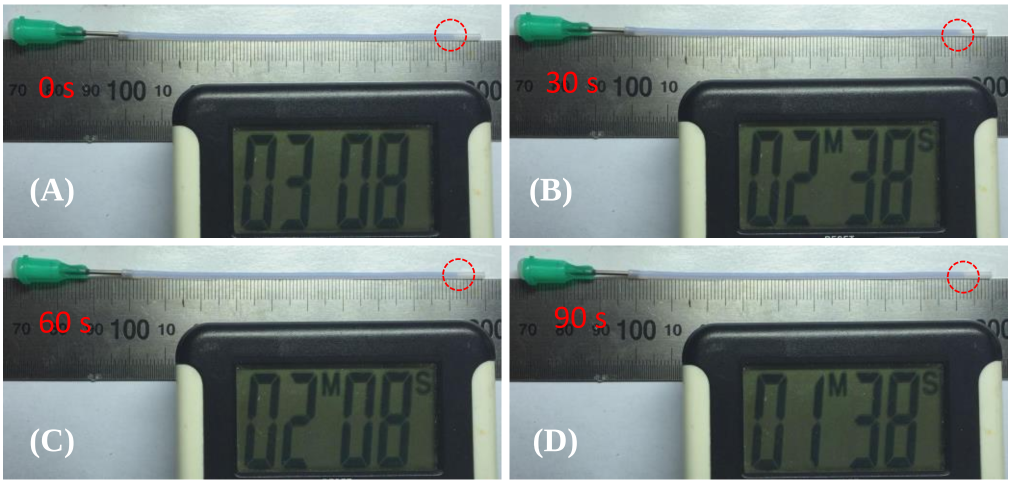


Figure S2. The solvent evaporation testing in 10 cm PTFE tubes. (A-D) are the photos of meniscus position in PTFE tubes with an interval of 30 seconds.

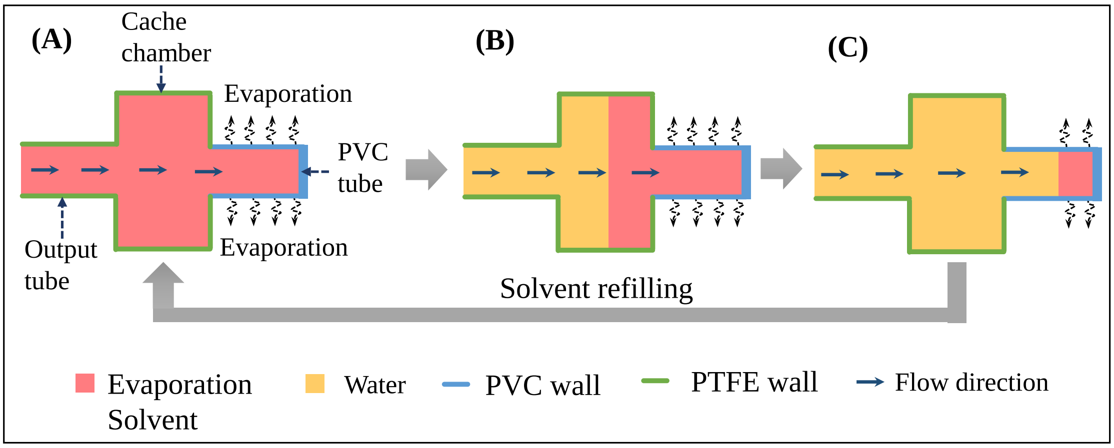


Figure S3. Schematic of fluid delivery using the evaporation pump. The system is filled with evaporation solvent, and one end of the PVC tube is blocked by the sealing plug (A). The solvent continuously diffuses into the surrounding environment via PVC wall, resulting in that the pressure in the system is reduced and water solution are sucked into the system (B). The solvent in the cache chamber flows back into the PVC tube to ensure constant evaporation area until the solvent is exhausted (C).

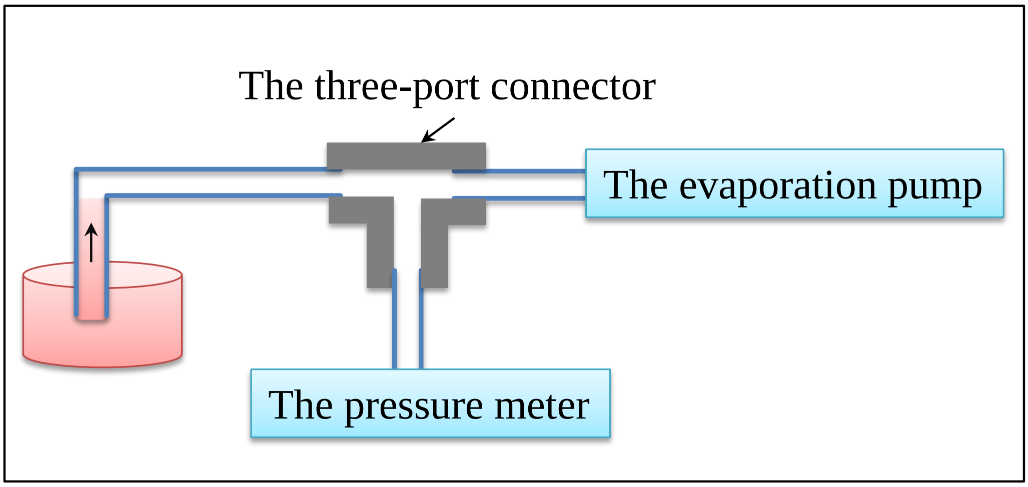


Figure S4. Schematic of the fluid delivery system used in pressure measurement. Fluid is driven by the evaporation pump.

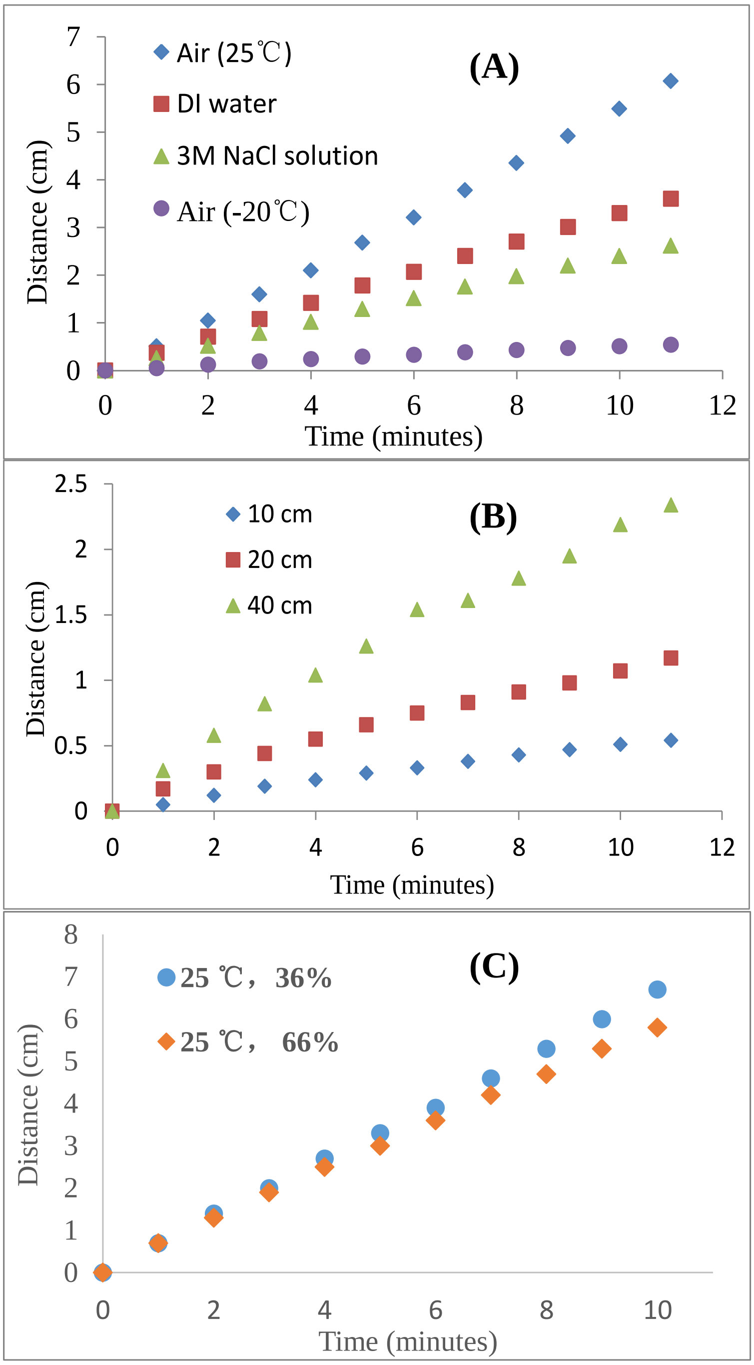


Figure S5. The investigation of pumping velocities at different environments. (A) The moving distance of meniscus in output tube from 0 to 11 minutes in different medium (air, DI water or high concentration salt solution) or temperatures (25 ℃ or -20 ℃). The EPt length is 10 cm. (B) The moving distance of meniscus in output tube from 0 to 11 min in refrigerator (-20℃) with different EPt lengths (10 cm, 20 cm or 40 cm). (C) The moving distance of meniscus from 0 to 10 minutes with relative humidity of 36 % and 66 %. The EPt length is 10 cm and the temperature is 25 ℃.

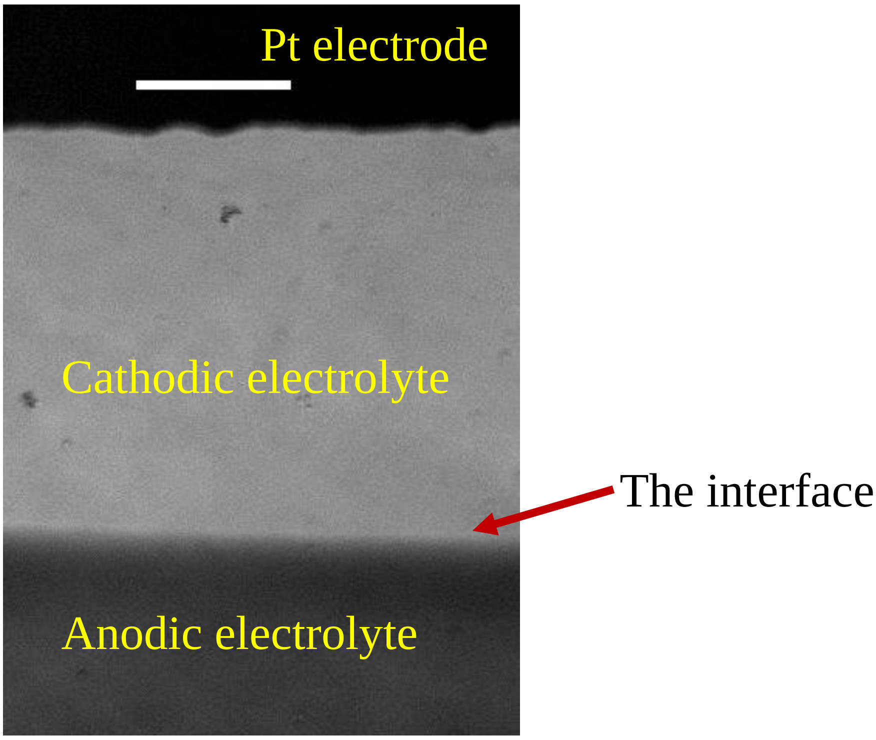


Figure S6. The micrograph of laminar flow formed by the evaporation pump with 40 cm EPt. Scale bar is 160 μm.

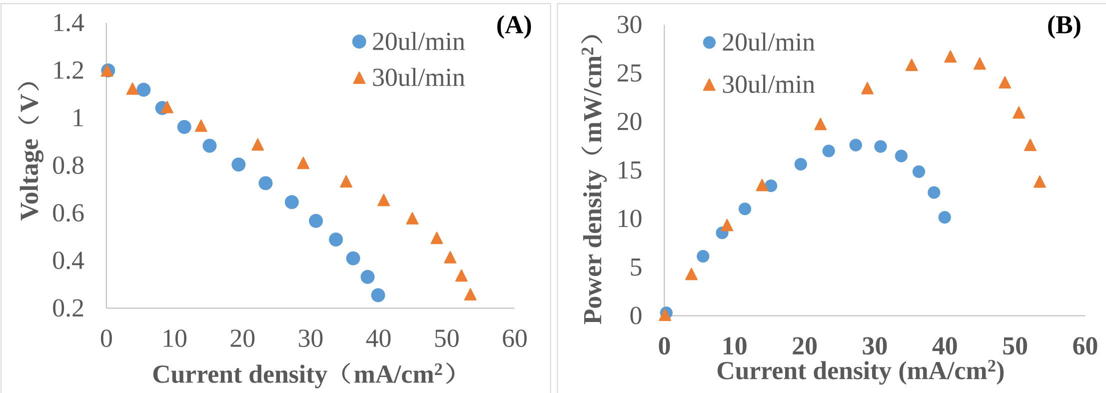
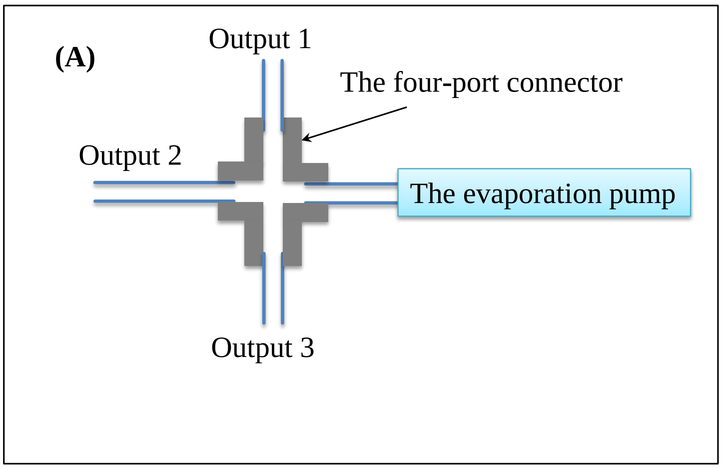


Figure S7. The steady-state polarized curves (A) and the power density curves of the cells driven by two syringes pumps under different flow rates. The anodic and cathodic electrolytes are pushed into the cell with identical flow rate (20 mL/min or 30 mL/min).



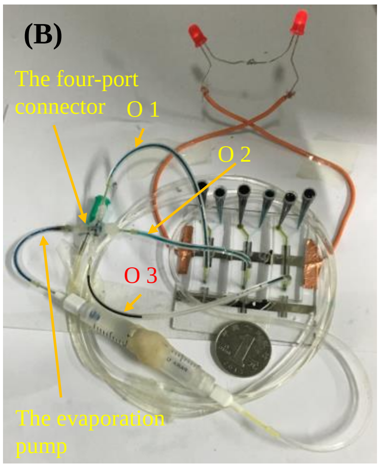


Figure S8. (A) Schematic of fluid delivery system with a four-port connector. (B) Two LEDs are lighted by installing three cells in series. The three cells are driven by the evaporation pump shown in (A).

References:
[1] Q. Zhang, X. Liu, D. Liu, H. Gai, Lab on a chip, 2014, 14, 1395–1400.
[2] R. Ferrigno, A. D. Stroock, T. D. Clark, M. Mayer and G. M. Whitesides, J. Am. Chem. Soc., 2002, 124, 12930-12931.