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RESEARCH PAPER

A flexible precise volume sensor based on metal-on-polyimide electrodes sandwiched by PDMS channel for microfluidic systems

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Abstract

This paper reports a flexible precise volume sensor with metal-on-polyimide (PI) electrodes to substitute for the peripheral ration pump of a microfluidic system, thus beneficial for integration and miniaturization. This in-channel volume sensor consists of multi-electrode pairs, and it can perform volume measurement of the fluid flowing through microchannels by testing the resistance variation of the electrode pairs, which makes the device possible to help automatically control the sample volume in the mixing and reacting processes inside a microfluidic chip without peripheral ration pumps. The electrode pairs of the sensor are fabricated on flexible PI surface directly by inkjet printing. Then, the electrodes with the PI substrate are transferred and sandwiched by a polydimethylsiloxane (PDMS) substrate layer and a PDMS channel layer to form the flexible precise volume sensor. This method overcomes the challenge of patterning metals on PDMS and the sandwiched PDMS–PI–PDMS structure is beneficial for integration with other PDMS-based microfluidic chips. The effects of electrode-tip shapes and numbers of the electrode pairs are also investigated. A novel calculating method is proposed to obtain more precise results when different numbers of electrode pairs are used in different situations. According to the experimental results, the more electrode pairs are used in the same spacing, the better measurement precision can be obtained. The volume sensor with optimized electrode-tip and multi-electrode pairs can detect the fluid volume in nanolitre scales with the relative error of $<0.8\%$. This work exhibits the potential to form a total lab-on-a-chip without peripheral ration pumps.

Keywords Volume sensor · Flexible microfluidics · Total lab-on-a-chip · Inkjet printing

1 Introduction

Microfluidic systems hold many advantages such as small sample and reagent consumption, mass and heat transfer efficiently, good biocompatibility, high-throughput parallel analysis, functional unit integration, miniaturization, and automation control. (Zhang et al. 2016) Thus, microfluidics is widely used in various fields, such as environment detection (Piaskowski et al. 2017), cell biology (Gencturk et al. 2017), protein analysis (Wade et al. 2017) and gene engineering (Gach et al. 2017). Unfortunately, although microfluidic chips could be highly integrated and miniaturized, the supporting peripheral devices are necessary and hold large sizes (Osaki et al. 2018), which are inconvenient for the integration and miniaturization of microfluidic systems. When it comes to implantable microfluidics, for example, the microfluidic blood vessel scaffold (Kappings et al. 2018), the peripheral devices must be removed to make a total chip. Besides, flexible microfluidics attract focuses recently because it may be used in wearable devices (Gao et al. 2019), obviously, for wearable applications, a total flexible chip without peripheral devices hold great significance.

The ration pump, an important peripheral device, is always used to input certain volumes of samples into microchannels. But, as mentioned above, it also significantly affects the integration and miniaturization of microfluidic systems. Besides, it is still a big challenge

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to directly detect and automatically control the injection volume of fluid into a microfluidic chamber for mixing and reacting (Okamoto and Ukita 2017). Therefore, a flexible precise volume sensor, which can be integrated with a flexible microfluidic chip, is required to substitute for the peripheral ration pump to automatically control the sample volume.

Nowadays, most of the volume sensors are based on thermal conduction (Harada et al. 2017; Shikida et al. 2016), however, the response of this kind of sensor depends on the temperature of the fluids; thus, environmental temperature control or compensation is required (Kuo et al. 2012; Silvestri and Schena 2012; Shikida et al. 2017). The thermal volume sensors are limited by the volume velocity due to the restriction of the temperature change response rate (Steiner et al. 2016). Additionally, the thermal volume sensors are restricted to the temperature-dependent fluids, for example, the fluids with protein cannot be heated to enable measurement. Some other volume sensors, for example, fiber grating volume sensor is also susceptible to temperature variation (Shen et al. 2018); Coriolis mass volume sensor needs calibration every time and is only applicable to rectangle channels, besides, this kind of sensor needs moving parts that make complex structure (Alveringh et al. 2018); piezoresistive fluid sensor exhibits low sensitivity and long response time (Tian et al. 2018). Therefore, in this paper, an electrode-based volume sensor, which performs volume measurement by testing the resistance variation of the electrode pairs when fluids arrive and depart, is proposed to overcome the present limitations.

Polydimethylsiloxane (PDMS), a flexible, transparent and elastic material, is widely used in microfluidics because of its remarkable biocompatibility and easy workability (Li et al. 2018). However, most of the present electrode-based volume sensors are fabricated on a glass/silicon and then bonded to PDMS-based microfluidic channel because it is difficult to directly fabricate microelectrodes on PDMS, which is hydrophobic and has weak adhesion to metals (Wu et al. 2015). But such electrode-based volume sensors are rigid and thus not suitable for a flexible microfluidic chip. In our previous work, we tried to mix sliver powders with PDMS to fabricate the volume sensor and integrate it with the PDMS-based microfluidic chip (Yu et al. 2012). This method enabled the fabrication of the flexible PDMS-based microfluidic chip, however, the shape of the electrode-tip varied greatly, which significantly affected the detection precision. Besides, the conductivity of the electrodes was low due to the dielectric PDMS among the silver powders. We also tried to fabricate electrodes on PDMS directly after surface modification by inkjet printing (Wu et al. 2015). This method enabled facile fabrication of electrodes on PDMS surface directly, however, the printed electrodes easily fell off from the PDMS substrate when they were electrified in electrolyte solution, significantly affecting the application to fluids.

In this paper, a flexible metal-on-polyimide (PI) in-channel volume sensor consisting of multi-microelectrode pairs is designed and fabricated for flexible microfluidics. A novel calculating method is proposed to obtain more precise results when different numbers of electrode pairs are used in different situations. The electrodes of the sensor are directly fabricated on the flexible PI film due to its remarkable adhesion to metals and high temperature resistance. (Hoang et al. 2016; Fang et al. 2016; Phan et al. 2019; Won et al. 2019). Then, the electrodes with the PI film are transferred and sandwiched by a PDMS substrate layer and a PDMS channel layer to form the flexible precise volume sensor. The sensor can help automatically control the sample volume in the mixing and reacting processes inside a microfluidic chip to substitute for the peripheral ration pumps. The sandwiched PDMS–PI–PDMS structure makes the sensor conveniently integrated with PDMS-based microfluidic systems. The electrode-based device makes it easy to be miniaturized. The detection principle of the sensor makes it insusceptible to temperature, applicable to various shapes of channels and have a quick response. The volume sensor holds simple structure and the fabricated electrodes exhibit robust contact with PI during electrification in the electrolyte solution. Additionally, this sensor is fabricated by inkjet printing, a low-cost direct writing micromanufacturing technique (Pu et al. 2018), which enables fabricating conformable shape of electrode-tip that is beneficial for volume detection accuracy.

2 Methods and materials

2.1 Design and fabrication of the flexible precise volume sensor

The flexible precise volume sensor, as shown in Fig. 1a, consists of a PDMS channel layer, a PDMS substrate layer and a sandwiched metal-on-PI electrode pairs located in the microfluidic channel. The multi-electrode pairs are directly printed on the PI film due to its remarkable adhesion to metals and high temperature resistance. Each pair of electrodes is separated by a small gap inside the channel such that fluid flowing through the channel will bridge the gap and then approach the measurement.

Figure 1b shows the photos of the fabricated flexible precise volume sensor. The flexible device is fabricated based on inkjet printing, PI transfer and bonding. Detailed fabrication procedures are demonstrated in Fig. 1c. First, a thin layer PDMS is spin-coated on the glass after treated by O_2 plasma (plasma device, Tonson Tech Automation Equipment Co., Ltd., China, 30 W, 30 mL/min, 18 Pa and 30 s), followed by heating for 30 min under 95 °C to cure

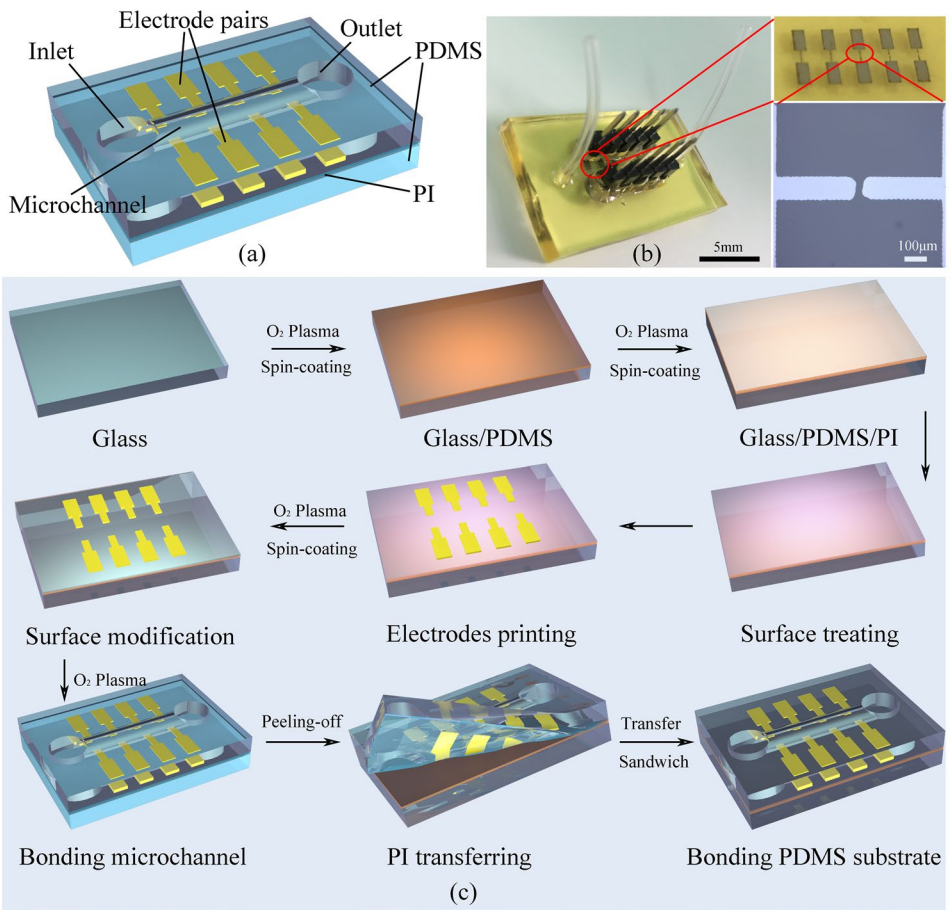

Fig. 1 Design and fabrication of the flexible precise volume sensor. **a** Schematic of the proposed precise volume sensor; **b** photos of the fabricated flexible volume sensor, the fabricated electrode pairs, and the electrode-tip; **c** manufacturing procedures of the flexible precise volume sensor

the spin-coated PDMS. O_2 plasma is used to treat the glass before spin-coating PDMS to enhance the adhesive of glass to PDMS, thereby avoiding the edge lifting of spin-coated PI when cured in high temperature. Second, after treating the PDMS surface by O_2 plasma (30 W, 30 mL/min, 18 Pa and 30 s), the PI film is spin-coated on it, followed by heating for 2 h under 250 °C to cure the spin-coated PI. Then, treat the PI surface by O_2 plasma (30 W, 30 mL/min, 18 Pa and 30 s) and keep it under room temperature for 48 h. Afterward, the electrode pairs of volume sensor are inkjet printed on the PI substrate, followed by heating for 2 h under 200 °C. Finally, the electrodes loading on the PI film is transferred from the glass/PDMS substrate and sandwiched by a PDMS substrate layer and a PDMS channel layer to form the flexible volume sensor after decorating the PI film surface with poly[dimethylsiloxane-co-(3-aminopropyl)methylsiloxane] (PDMS-linker). The PDMS channel layer is fabricated based on the traditional soft lithography method (Kim et al. 2017).

2.2 Surface treatment

As shown in Fig. 1c, the PI film is treated by O_2 plasma before printing the electrodes. The pre-treatment makes the PI surface more hydrophilic, which is beneficial for the dispersion of inkjet droplets (Wu et al. 2015). This method avoids coalescence of adjacent droplets to form durable electrodes. Figure 2a, b shows the topography of the PI surface before and after O_2 plasma treatment. As demonstrated in the AFM images, the treated PI surface is rougher at the nanoscale, which makes it more hydrophilic. As illustrated in Fig. 2c, d, the diameter of the droplets on the treated PI film is larger than those on the untreated PI film. This phenomenon verifies that the PI film is more hydrophilic after O_2 plasma treatment. Figure 2e, f shows photos of the lines printed on the treated and untreated PI film, respectively. The two photos verify that the O_2 plasma treatment method before printing avoids the coalescence of adjacent droplets to help form electrodes with desired shapes.

PDMS-linker is used to decorate the PI film surface to enable it bond to PDMS layer to form the sandwiched structure. The PDMS-linker is first spin-coated on the PI surface, followed by keeping the coated film under the room temperature at atmosphere for 20 min. Then rinse it with isopropyl alcohol and make an ultrasound bath for 90 s to completely remove the free PDMS-linker molecules.

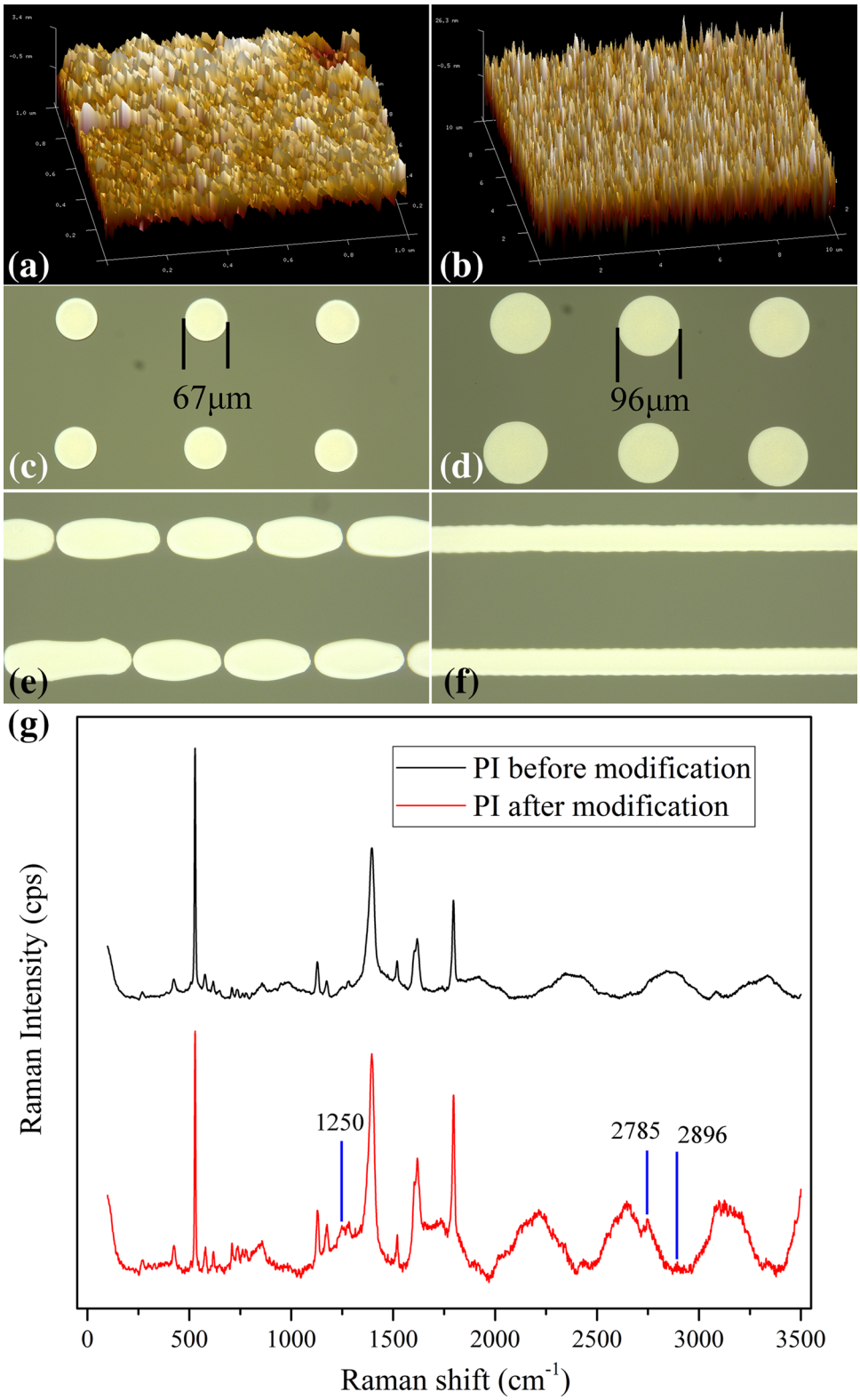

Fig. 2 Surface treatment for PI film. AFM images of PI surface before (**a**) and after (**b**) treatment; droplets disperse on PI surface before (**c**) and after (**d**) treatment; photos of the printed lines on PI surface before (**e**) and after (**f**) treatment; **g** Raman spectroscopy of PI surface before and after treatment

After drying with air stream, the PI film is bonded to the prepared PDMS layers. Figure 2g shows the Raman spectroscopy of the PI surface before and after decoration with PDMS-linker after O_2 plasma treatment (100 W, 30 mL/min, 18 Pa and 30 s). The peaks at 1250, 2785 and 2896 cm^{-1} ($–CH_3$) indicate successful modification.

2.3 Methods of volume measurement

The working principle of this precise volume sensor is similar to that described in our previous work (Yu et al. 2012). Briefly, as shown in Fig. 3, a conductive fluid flowing through the channel will bridge the gap and cause the resistance between the electrodes sharply decrease. Then, the volume can be calculated by detecting the resistance change time of the electrode pair when the interface between the two fluids with different conductivities flow through the gap of the electrode tips. That is to say, as long as there is a distinct interface between two fluids (one for measured, one for the encapsulating matrix) which have different conductivities, the method can be used. If some valves were integrated with this sensor, we can control the input sample volume according to the resistance jumping signal from the electrode pairs without a peripheral ration pump. Thus, the volume sensor exhibits the possibility to help automatically control the sample volume in the mixing and reacting processes inside a microfluidic chip without peripheral ration pumps.

When different numbers of electrode pair are used to calculate the fluid volume, different formulas are used accordingly. When only one electrode pair (E_1) is used, the volume can be calculated from formula (1):

$$V_1 = v \cdot (t_2 - t_1) \cdot W \cdot H, \tag{1}$$

where V_1 represents the volume of the fluid; v represents the flow rate of the fluid required on this condition (obtained from the fluidic driving device, for example, peristaltic pump); t_1 and t_2, respectively, represent the time for the head and the tail of the fluid to flow through the electrode pair E_1; W and H represent the width and height of the microfluidic channel which can be designed by users (a rectangle microchannel is used in this work). In this work, the W and H are fabricated as 700 μm and 230 μm, respectively. Smaller size of microchannel could enable the measurement for smaller volume of fluids.

Unfortunately, to our knowledge, the flow rates of microfluids fluctuate whichever the precise peristaltic pump used, and many frequently used peristaltic pumps cannot set a certain fluid flow rate. Therefore, in this paper, multi-electrode pairs are used to detect the arrival/departure time of the fluidic flow, thereby calculating the flow rate, which, in turn, to calculate the volume. The calculated flow rate is closer to the actual flow rate compared with the set one from the peristaltic pump. When more electrode pairs are used in the same spacing, the more precise flow rate (volume) can be obtained because more effect of flow fluctuations will be reduced. Specifically, when different numbers of electrode pairs exist in the same length of microchannel, different formulas are used to calculate the volume to reduce the effect of flow fluctuations as much as possible. In this paper, 1, 2, 3, 5 electrode pairs in the same length of microchannel are used to calculate the fluid volume, separately. As the volume to be detected is different, the time sequence of t is different accordingly.

If $t_2 \leq t_3$ ($V \leq 0.4025$ μL in our chip), when two electrode pairs (E_1 and E_5) are used, the volume is calculated from formula (2):

$$V_{1,5} = \frac{4S}{t_9 - t_1} \cdot (t_2 - t_1) \cdot W \cdot H, \tag{2}$$

where $V_{1,5}$ represents the volume of the fluid; $4S$ represents the length between E_1 and E_5; t_9 represents the time for the head of the fluid to flow through the electrode pair E_5. At this situation, the flow rate of the fluid is not necessary because it can be calculated by $4S/(t_9 - t_1)$. In this paper, S is designed as 2.5 mm. When three electrode pairs (E_1, E_3 and E_5) are used, the volume is calculated from formula (3):

$$V_{1,3,5} = \frac{2S}{t_5 - t_1} \cdot (t_2 - t_1) \cdot W \cdot H, \tag{3}$$

when five electrode pairs (E_1, E_2, E_3, E_4 and E_5) are used, the volume is calculated from formula (4):

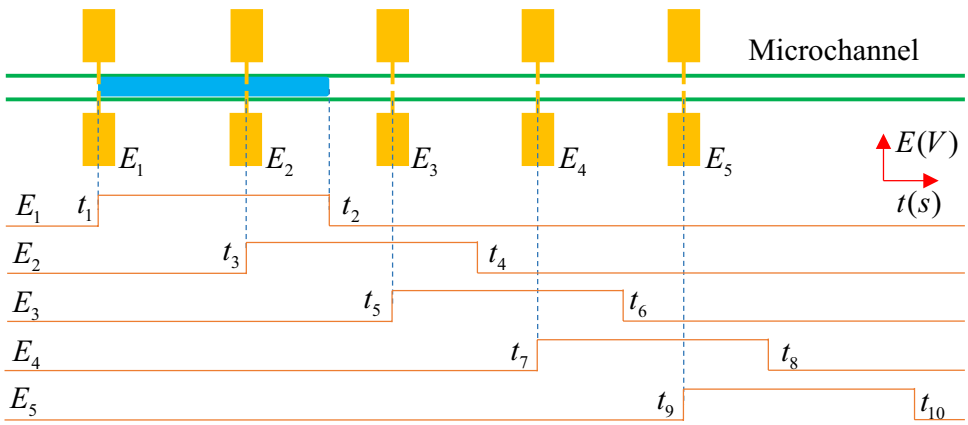

Fig. 3 Schematic diagram of the working principle of the proposed flexible volume sensor

$$V_{1,2,3,4,5} = \frac{S}{t_3 - t_1} \cdot \left(t_2 - t_1\right) \cdot W \cdot H. \tag{4}$$

Similarly, if $t_3 \le t_2 \le t_5$ ($0.4025 \le V \le 0.805$ μL in our chip), when two electrode pairs (E_1 and E_5) or three electrode pairs (E_1, E_3 and E_5) are used, the volume can also be calculated from formulas (2) or (3), respectively. While for five electrode pairs (E_1, E_2, E_3, E_4 and E_5), the volume is calculated from formula (5):

$$V_{1,2,3,4,5} = S \cdot W \cdot H + \frac{S}{t_3 - t_1} \cdot \left(t_2 - t_3\right) \cdot W \cdot H, \tag{5}$$

if $t_5 \le t_2 \le t_7$ ($0.805 \le V \le 1.2075$ μL in our chip), when two electrode pairs (E_1 and E_5) are used, the volume can be calculated from formula (2). While for three electrode pairs (E_1, E_3 and E_5) and five electrode pairs (E_1, E_2, E_3, E_4 and E_5), the volume is calculated from formulas (6) and (7), respectively:

$$V_{1,3,5} = 2S \cdot W \cdot H + \frac{2S}{t_5 - t_1} \cdot \left(t_2 - t_5\right) \cdot W \cdot H. \tag{6}$$

$$V_{1,2,3,4,5} = 2S \cdot W \cdot H + \frac{S}{t_5 - t_3} \cdot \left(t_2 - t_5\right) \cdot W \cdot H, \tag{7}$$

if $t_7 \le t_2 \le t_9$ ($1.2075 \le V \le 1.61$ μL in our chip), when two electrode pairs (E_1 and E_5) or three electrode pairs (E_1, E_3 and E_5) are used, the volume can be calculated from formulas (2) or (6), respectively. While for five electrode pairs (E_1, E_2, E_3, E_4 and E_5), the volume is calculated from formula (8):

$$V_{1,2,3,4,5} = 3S \cdot W \cdot H + \frac{S}{t_7 - t_5} \cdot \left(t_2 - t_7\right) \cdot W \cdot H, \tag{8}$$

if $t_2 \ge t_9$ ($V \le 2.0125$ μL in our chip), for two electrode pairs (E_1 and E_5), three-electrode pairs (E_1, E_3 and E_5) and five electrode pairs (E_1, E_2, E_3, E_4 and E_5), the volume is calculated from formulas (9), (10) and (11), respectively:

$$V_{1,5} = 4S \cdot W \cdot H + \frac{4S}{t_9 - t_1} \cdot \left(t_2 - t_9\right) \cdot W \cdot H, \tag{9}$$

$$V_{1,3,5} = 4S \cdot W \cdot H + \frac{2S}{t_9 - t_5} \cdot \left(t_2 - t_9\right) \cdot W \cdot H, \tag{10}$$

$$V_{1,2,3,4,5} = 4S \cdot W \cdot H + \frac{S}{t_9 - t_7} \cdot \left(t_2 - t_9\right) \cdot W \cdot H. \tag{11}$$

Different equations are used to calculate the volumes in different ranges to reduce the effect of flow fluctuations on the volume measurements as much as possible. For example, if $t_3 \le t_2 \le t_5$ ($0.4025 \le V \le 0.805$ μL in our chip), the length of the fluid is longer than the distance between two adjacent electrode pairs (S) while shorter than the distance covered by three adjacent electrode pairs ($2S$). When five electrode pairs are used to calculate the volume from formula (5), the fluid is divided to be measured into two parts: one part fulfills with the volume between two adjacent electrode pairs and the other smaller part cannot fulfill with the volume between two adjacent electrode pairs. At this situation, the effect of flow fluctuations can be reduced from the whole fluid ($> S$) to a small part of it ($< S$), thereby achieving more precise measurement. While for $t_5 \le t_2 \le t_7$ ($0.805 \le V \le 1.2075$ μL in our chip), the length of the fluid is longer than the distance covered by three adjacent electrode pairs ($2S$) while shorter than the distance covered by four adjacent electrode pairs ($3S$). If still use Eq. (5) to calculate the volume, the effect of flow fluctuations is only reduced from the whole fluid ($> 2S$) to a part of it ($< 2S$ while $> S$). While if use Eq. (7) to calculate the volume, the effect of flow fluctuations can be reduced to a smaller part of it ($< S$), which gets more precise result. Similarly, if $t_7 \le t_2 \le t_9$ ($3S \le$ the length $\le 4S$ in our chip), when two electrode pairs (E_1 and E_5), three electrode pairs (E_1, E_3 and E_5) and five electrode pairs are used, the volume can be calculated from formulas (2), (6) and (8), respectively. The effect of flow fluctuations can be reduced from the whole fluid ($> 3S$) to a part of them ($< 2S$ while $> S$) and ($< S$), respectively. Therefore, the formulas using denser electrode pairs should be used based on the fluid length (the length can be determined by the value of t_2) to achieve more precise measurements.

3 Results and discussion

3.1 Measurement system

A schematic diagram of the measurement system for the characterization of the proposed volume sensor is shown in Figure S1. A peristaltic pump (SMP-21S, Tokyo Rikakikai Co., Ltd., Japan) is used to provide the pressure to drive the fluid flowing through the microfluidic channel. When the volume sensor proposed in this paper is integrated with other systems for application, the peristaltic pump can be substituted by on-chip pumps such as the self-sufficient pressure pump (Thurgood et al. 2018). Five 10 MΩ resistors (R_1, R_2, R_3, R_4 and R_5) and five pairs of electrodes (E_1, E_2, E_3, E_4 and E_5) are connected in series, respectively. A 1 V, 100 Hz AC voltage (supported by a data acquisition interface, NI USBM6259, National Instruments, Inc., USA) is then applied to these five series circuits. The voltage change across a 10 MΩ resistor represents the resistance change of its corresponding electrode pair. Following signal conditioning (impedance reduction and 60 Hz noise filtering), the voltage data are input into the computer through the data acquisition interface (NI USBM6259, National Instruments,

Inc., USA). The sampling frequency of the data acquisition interface is set to be 1 kHz. During the fluid flowing, the voltages on all five resistors are measured, and the time of the voltage change are used to calculate the volume of the fluid. In this paper, some peripheral setups are used to characterize the volume sensor, including the inlet, connections from electrodes to a measurement system and the measurement system. While for the real applications, the inlet is able to connect to the microchannel of other chips needing volume sensing/control; the measurement/control system can be substituted by a small integrated chip to miniaturize the device; the connections from electrodes to the measurement/control system can also be miniaturized to integrate with the small integrated chip.

3.2 Effect of the shape of electrode tip

As the rising and falling edge steepness of the time-varying resistance signal of the volume sensor depends on the geometry of electrode tip, as shown in Fig. 4a, eight kinds of electrode tips are designed and printed to optimize the volume sensor. The rising and falling edges of the voltage signals converted from the resistance signals of the eight kinds of electrodes are recorded and shown in Fig. 4b. The measurement results indicate that the 33° and 150 µm electrode tips get the steepest rising and falling edges of the signals, which are beneficial for the detection of the exact time that the fluid flows through the electrode pairs and thus effectively improving the volume measurement precision. However, owing to the small size of the microchannel, it is difficult to bond the electrodes layer to the microchannel layer while keeping the symmetry of the two tips in the microchannel. For the triangular electrode tip, the symmetry of the two tips dramatically affects the measurement precision of the change time because one of the tips would have a much bigger tail than the other one if had a bonding error. Additionally, the signal of the 150-µm electrode tip is the most stable one which is beneficial for the signal sampling and application. Therefore, the elongated 150-µm electrode tip was selected finally considering both the steep edge of signal and the fabrication difficulty.

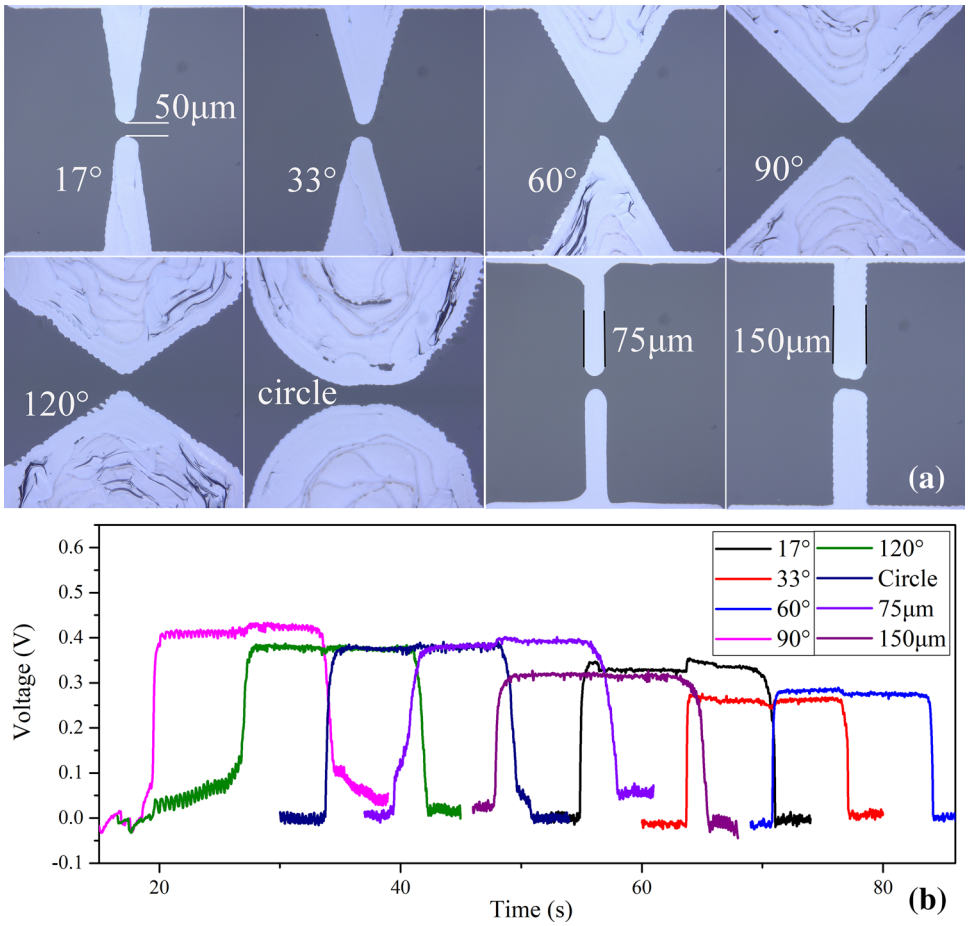

Fig. 4 Effect of the shape of electrode tip. **a** Photos of the printed eight kinds of electrode tip; **b** readouts of the different kinds of electrode tips

3.3 Effect of the numbers of electrode pairs

After obtaining the optimized shape of electrode tip, we designed and fabricated different numbers of electrode pairs to monitor the volumes of fluids. For the use of different numbers of electrode pairs, different formulas, as mentioned in the methods part, were used to calculate the fluid volumes. Table 1 shows the volumes calculated using different pairs of electrodes under different flow rates ($n = 10$). Table 2 shows the relative percentage error for the volumes calculated. The results are also shown in Fig. 5. In these experiments, the tested fluids are repetitive flowing through the microchannel of the device back and forth for 10 times. The first row of each table lists the initial actual volumes of the fluid portions. Before the testing, the fluid portions are injected into the inlet tube (inside diameter of 1 mm) by a microsyringe, then a vernier caliper with the accuracy of 0.02 mm is used to measure the length of the injected fluid portion. Afterward, the actual volume of the fluid portion is obtained. According to the results, the flow rate changing in the range of 5–20 μL/min has little effect on the measurement precision when the volume is more than 509 nL. According to Tables 1 and 2, when more electrode pairs are used in the same spacing, the better measurement precision can be obtained. Besides, according to the experimental results, even with the precise peristaltic pump, the volumes measured by one electrode pair and the set flow rate from the peristaltic pump is with much low precision than those by multi-electrode pairs only. Additionally, all of the results for one pair of electrodes are smaller than the actual volumes, which may be caused by the systematic error of using the flow rates from the peripheral ration pump. Therefore, the volume measurement based on multi-electrode pairs is promising for frequently used fluid driving methods which can hardly control the fluidic flow rate precisely.

Table 2 Relative percentage error for the volumes measured under different flow rates ($n = 10$)

Volume (μL)	Using different numbers of electrode pairs			
	1 (%)	2 (%)	3 (%)	5 (%)
The volumes measured under the flow rate of 5 μL/min				
0.3694	11.61	0.27	0.70	0.89
0.5092	10.51	0.11	0.08	0.02
0.9874	9.83	0.78	0.33	0.16
1.4902	11.60	0.24	0.16	0.04
1.9600	10.69	0.01	0.02	0.01
The volumes measured under the flow rate of 10 μL/min				
0.3014	7.73	1.99	0.83	0.80
0.6451	9.41	0.31	0.26	0.22
1.1081	10.00	0.92	0.52	0.51
1.5565	10.72	0.62	0.46	0.14
2.1106	10.53	0.02	0.02	0.01
The volumes measured under the flow rate of 20 μL/min				
0.2908	9.18	2.68	1.31	3.13
0.5982	10.35	0.47	0.32	0.27
1.0429	10.96	1.07	0.60	0.50
1.3614	12.94	0.17	0.18	0.11
2.0743	13.08	0.05	0.06	0.04

Table 1 Results by different numbers of electrode pairs under different flow rates ($n = 10$)

Volume (μL)	Using different numbers of electrode pairs			
	1	2	3	5
Volumes measured under the flow rate of 5 μL/min				
0.3694	0.3265 ± 0.0124	0.3684 ± 0.0132	0.372 ± 0.0134	0.3661 ± 0.0069
0.5092	0.4557 ± 0.0142	0.5097 ± 0.0155	0.5088 ± 0.0151	0.5091 ± 0.0126
0.9874	0.8903 ± 0.0114	0.9951 ± 0.0116	0.9841 ± 0.0085	0.9858 ± 0.0099
1.4902	1.3174 ± 0.0641	1.487 ± 0.0721	1.4926 ± 0.0791	1.4908 ± 0.0719
1.9600	1.7504 ± 0.0282	1.9598 ± 0.0296	1.9603 ± 0.0304	1.9599 ± 0.0298
Volumes measured under the flow rate of 10 μL/min				
0.3014	0.2781 ± 0.0109	0.3074 ± 0.0097	0.2989 ± 0.0128	0.2990 ± 0.0132
0.6451	0.5844 ± 0.0065	0.6471 ± 0.0074	0.6434 ± 0.0073	0.6437 ± 0.003
1.1081	0.9973 ± 0.0084	1.1183 ± 0.0075	1.1023 ± 0.006	1.1025 ± 0.0047
1.5565	1.3897 ± 0.0472	1.5662 ± 0.0158	1.5494 ± 0.036	1.5587 ± 0.0164
2.1106	1.8883 ± 0.0268	2.111 ± 0.0131	2.111 ± 0.0142	2.1109 ± 0.0133
Volumes measured under the flow rate of 20 μL/min				
0.2908	0.2641 ± 0.0174	0.2986 ± 0.0191	0.2946 ± 0.0262	0.2817 ± 0.0147
0.5982	0.5363 ± 0.0115	0.6010 ± 0.0126	0.5963 ± 0.0167	0.5966 ± 0.0172
1.0429	0.9286 ± 0.0198	1.0541 ± 0.0228	1.0366 ± 0.0247	1.0377 ± 0.0242
1.3614	1.1852 ± 0.097	1.3591 ± 0.1136	1.3638 ± 0.1156	1.3629 ± 0.1109
2.0743	1.8030 ± 0.0369	2.0732 ± 0.0575	2.0755 ± 0.0556	2.0734 ± 0.0572

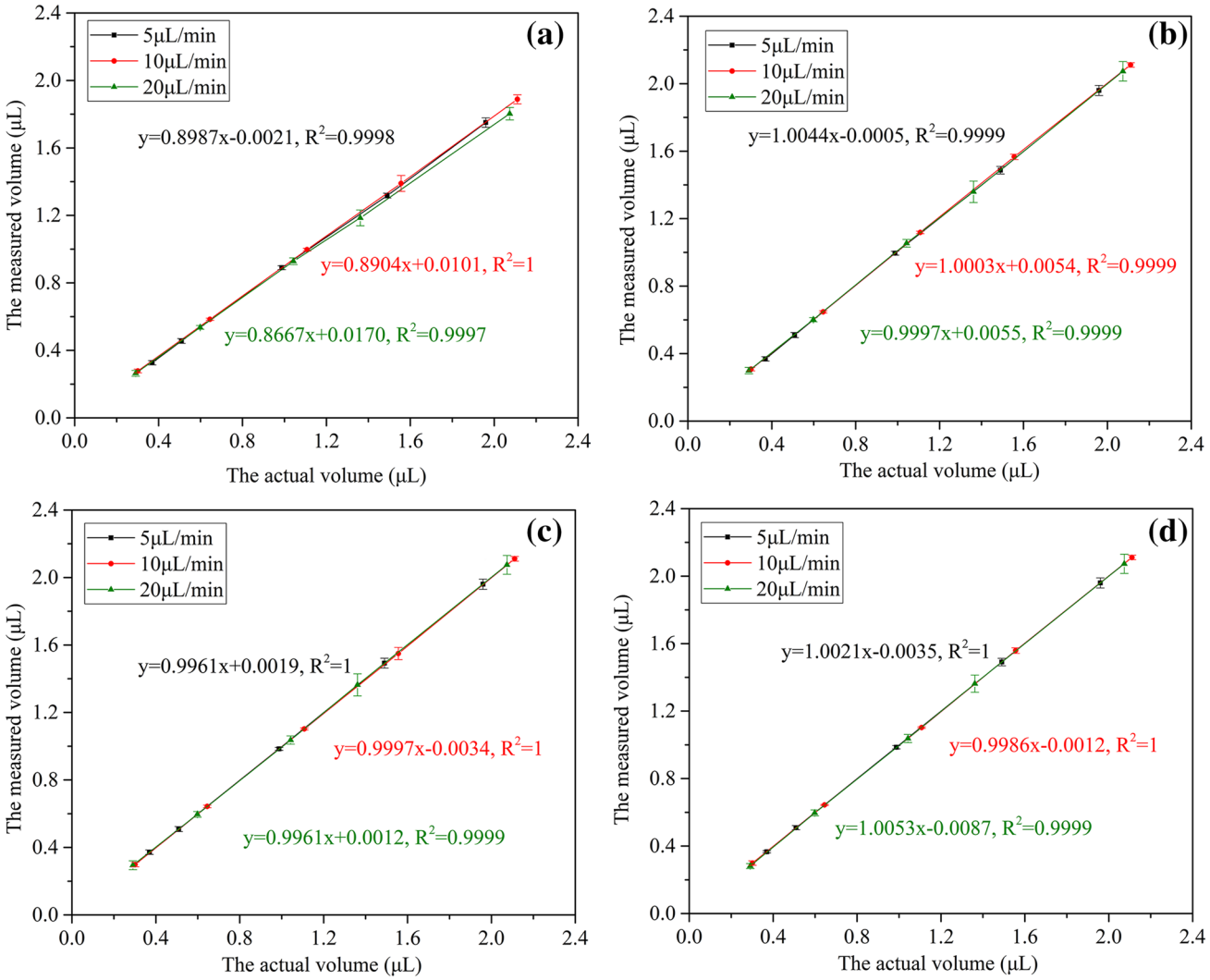

Fig. 5 A comparison of the measured volumes using different number of electrodes at three flow rates ($n = 10$). **a** One electrode pair; **b** two electrode pairs; **c** three electrode pairs; **d** five electrode pairs

When the flow rate is lower than 10 μL/min, the relative error of the results obtained from five electrode pairs can be lower than 0.8% even the volume of the fluid is as small as 301 nL. These results exhibit the fabricated sensor can precisely determine the fluid in nanolitre scales which indicates the fabricated volume sensor has the potential to help automatically control the nanolitre scale's sample volume in the mixing and reacting processes inside a microfluidic chip.

Additionally, as shown in Tables 1 and 2, although most of the results exhibit the idea that the more electrode pairs are used the better measurement precision can be obtained, when the volume of the fluid to be detected is less than 0.4025 μL, it does not match the idea. This phenomenon may be caused by the fluid hanging during the repetitive fluid flowing. Simultaneously, according to Tables 1 and 2, higher flow rate makes worse measurement precision because more fluid will be hanged for faster flowing rates. Therefore, we conducted another volume measuring experiments which got the fluids flow through the microchannel of the flexible volume sensor only once. The results of calculated volumes and the corresponding relative percentage error are shown in Table S1 and Table S2, respectively. According to the two tables, the idea, the more electrode pairs are used in the same spacing the better measurement precision can be obtained, is verified even the volume of fluid to be detected is less than 0.4025 μL. Furthermore, if the spacing between two electrode pairs, i.e. S, reduces, more precise measurements can be achieved.

3.4 Lifetime test

In order to verify the fabricated flexible volume sensor can be used for a long time. After characterized the device for 1 day as soon as it was fabricated, we tested its property

Table 3 Comparison of results between as-fabricated and after 20 days saved ($n = 10$)

		Volume (μL)	Using numbers of electrode pairs			
			1	2	3	5
Recording results	As-fabricated	1.1081	0.9973 ± 0.0084	1.1183 ± 0.0075	1.1023 ± 0.006	1.1025 ± 0.0047
	20 days later	1.0922	1.0035 ± 0.0161	1.1029 ± 0.0082	1.1011 ± 0.0071	1.0942 ± 0.0055
Relative percentage error	As-fabricated	1.1081	10.00%	0.92%	0.52%	0.51%
	20 days later	1.0922	8.12%	0.98%	0.81%	0.18%

20 days later (the device was kept under the room temperature at atmosphere for this period). The results for the two tests under the flow rate of 10 μL/min are compared and demonstrated in Table 3. These results indicate that the fabricated volume sensor has a long lifetime with maintained measurement precision.

Particularly, the flexible volume sensor is developed for flexible applications. Thus, we bent the device more than 10 times for more than 90° before connecting the wires, then made the fluid detection experiments. The experimental results exhibit that the several times bending did not destroy the device. Similarly, for the life time test, the device was bent for many times as well, the performance of the device kept well after bending.

Besides, for the application of several fluid portions in series, as long as there are distinct interfaces between each fluid portion and its encapsulating matrix, and the two fluids have different conductivities, when several fluid portions flow through the channel in series, several resistance change time can be detected, then the volume of every fluid portion can be measured in series.

Additionally, distilled water (pH 7) encapsulated by air is used as the fluid portions to be measured in this paper. For the application to other fluids, too high or too low pH may destroy the Ag electrode, thereby affecting the application. Thus, other more stable conductive materials, for example, Au, may be used to form the electrode for application in the condition of too high or too low pH, the Au electrodes can be fabricated by inkjet printing as well.

4 Conclusions

In this paper, a flexible precise volume sensor consisting of metal-on-PI in-channel electrodes and two as-sandwiched PDMS layers is proposed to substitute for a peripheral ration pump of a microfluidic system. The electrode pairs of the sensor are fabricated on flexible PI film directly by inkjet printing, then the electrodes are transferred and sandwiched by two PDMS layers. This method overcomes the challenge of patterning metals on PDMS directly and the outside PDMS structure make the device beneficial for integration with other PDMS-based microfluidic chips. Before printing the electrodes, the PI film is pre-treated by O_2 plasma to make it more hydrophilic, which is beneficial for inkjet droplets to disperse on the PDMS surface. This method avoids coalescence of adjacent droplets to form durable electrodes. The volume sensor holds simple structure and the fabricated electrodes exhibits robust contact to PI during electrified in electrolyte solution. PDMS-linker is used to modify the PI surface to enable it bond to PDMS layers to realize the fabrication of the precise volume sensor with the sandwiched PDMS–PI–PDMS structure. Besides, the effects of electrode-tip shapes and numbers of electrode pairs are investigated. The 150 μm electrode tip demonstrates the best property for measurement precision.

A novel calculating method is proposed to obtain more precise results when different numbers of electrode pairs are used in different situations. According to the experimental results, the more electrode pairs are used in the same spacing, the better measurement precision can be obtained. With this method and the optimized structure of electrode tip, the fabricated flexible volume sensor can precisely detect the volume of fluid in nanolitre scales with the relative error of $< 0.8\%$, which indicates the device has the potential to help automatically control the nanolitre scale's sample volume in the mixing and reacting processes inside the microfluidic chip without peripheral ration pumps. This work exhibits the potential to form total micro-chips without peripheral devices.

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