A “place n play” modular pump for portable microfluidic applications

Gang Li,^{1,a)} Yahui Luo,^{1,2} Qiang Chen,¹ Lingying Liao,¹ and Jianlong Zhao^{1,a)}

¹State Key Lab of Transducer Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China

²Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

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This paper presents an easy-to-use, power-free, and modular pump for portable microfluidic applications. The pump module is a degassed particle desorption polydimethylsiloxane (PDMS) slab with an integrated mesh-shaped chamber, which can be attached on the outlet port of microfluidic device to absorb the air in the microfluidic system and then to create a negative pressure for driving fluid. Different from the existing monolithic degassed PDMS pumps that are generally restricted to limited pumping capacity and are only compatible with PDMS-based microfluidic devices, this pump can offer various possible configurations of pumping power by varying the geometries of the pump or by combining different pump modules and can also be employed in any material microfluidic devices. The key advantage of this pump is that its operation only requires the user to place the degassed PDMS slab on the outlet ports of microfluidic devices. To help design pumps with a suitable pumping performance, the effect of pump module geometry on its pumping capacity is also investigated. The results indicate that the performance of the degassed PDMS pump is strongly dependent on the surface area of the pump chamber, the exposure area and the volume of the PDMS pump slab. In addition, the initial volume of air in the closed microfluidic system and the cross-linking degree of PDMS also affect the performance of the degassed PDMS pump. Finally, we demonstrated the utility of this modular pumping method by applying it to a glass-based microfluidic device and a PDMS-based protein crystallization microfluidic device. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692770>]

I. INTRODUCTION

As an emerging technology, microfluidics has shown great potential in various areas such as biological and chemical analysis,^{1,2} medicine,^{3,4} biotechnology,^{5,6} and environmental monitoring.⁷ Microfluidic devices have numerous advantages over traditional laboratory analytical equipments, including reduced requirements for expensive reagents, short analysis times, increased sensitivity of analysis, and portability. However, in spite of these economic and scientific benefits, microfluidic devices have been relatively slow to propagate into actual applications, especially in the field of point-of-care diagnostics and some resource-limited applications or environments.^{8,9} One reason for this could be that these devices typically require bulky and expensive external hardware to initiate and control fluid flow. At present, traditional pumps such as syringe pumps, peristaltic pumps, and regulated source of pressure or vacuum are widely utilized in microfluidic systems. In addition, electrokinetic-driven pumping is one of the most popular methods in microfluidic transport. Though these pumps make a precise and reliable control of the fluid flow in microchannels, there are limitations of the portability owing to their size.¹⁰ In this regard, numerous research efforts have been made to develop various types of integrated micropumps for portable

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: gang_li@mail.sim.ac.cn and jlzhao@mail.sim.ac.cn.

microfluidic applications by utilizing piezoelectric,^{11–14} electrostatic,¹⁵ pneumatic,^{16,17} or magnetic effects.¹⁸ Although these on-chip pumps increase the device portability, integrating the pumping components (e.g., diaphragms, actuators, valves, and heaters) on the device significantly increases the fabrication complexity and device cost. As most microfluidic devices are made to be disposable to reduce contamination across samples, on-chip pumping is not always an attractive choice. Aimed at avoiding expensive and nondisposable active microfluidic pumps, several researchers have proposed some interesting portable pumping mechanisms, such as droplet-based passive pumping,¹⁹ evaporation,^{20–22} capillary flow,^{23,24} gravity-driven flow,^{25,26} and finger-actuated pumping.^{27,28} These developed portable micropumps scale rather favorably in microfluidics while preserving simplicity. However, they make the systems either complex to fabricate or difficult to provide precise and complicated fluidic control.

Recently, a more practical pumping method for portable microfluidic systems that requires neither any external power nor expensive on-chip microfluidic components has been proposed by Hosokawa and co-workers.²⁹ This pumping mechanism takes advantage of the inherent porosity and air solubility of PDMS. By evacuating the air dissolved in the bulk PDMS, the air concentration in PDMS decreases and the energy for the pumping is pre-stored in the degassed bulk PDMS. When the degassed PDMS microdevice is brought back to the atmosphere, a re-dissolution process of air into the PDMS takes place immediately. If a sample is loaded into the inlet port to form a closed channel-reservoir system, the re-dissolution of air through the microchannel walls results in a lower pressure inside the microchannel relative to the atmospheric pressure. Thus, the sample is drawn into the channels owing to this pressure difference. Recently, this passive pumping method has been used in various microfluidic applications, including immunoassays,^{30,31} gold nanoparticle-based DNA analysis,^{29,32,33} nanoliter-scale protein crystallization,³⁴ viscosity measuring,^{35,36} blood analysis,³⁷ and cell loading.³⁸ This on-chip degas-driven pumping method that is capable of running without any external power is simple and convenient for the end user. However, the degas-driven pumping capacity is relatively fixed for a given PDMS microfluidic chip, and the duration of the pumping activity is also short as the air distribution inside and outside the PDMS reaches the equilibrium soon after the degassed PDMS microchip is placed in atmosphere. More unfavorably, this monolithic pumping method is only compatible with PDMS microfluidic chips, which greatly limits its application scope in microfluidic systems.

To address the above limitations, we developed a modular degassed PDMS pump for portable microfluidic applications. In comparison with the classic monolithic approach to microfluidic systems, the modular approach offers increased system flexibility and reduced individual device fabrication complexity. This modular pump expands the application range of the degas-based pump from PDMS-based microfluidic devices to any material microfluidic devices. More importantly, it offers the advantages that the pump module could be wrapped in an air-tight packaging to meet the readily available requirements, and it also easily assembled, which only requires the user to place a pre-degassed PDMS pump slab on the outlet ports of a microchip. This reversible assembly provides great freedom for changing pump modules for adapting to different pumping requirements. Furthermore, this modular pump format can also offer many possible configurations of pumping power by varying the geometries of the pump or by combining different pump modules.

II. THEORY BACKGROUND

The working mechanism of the degassed PDMS pump is based on the absorption of air in a closed system into PDMS. This air absorption can be characterized as a solution–diffusion process.³⁹ First, air solution occurs at the surface of the degassed PDMS and then the dissolved air molecules diffuse into the interior of the PDMS. The solution process can be described in terms of Henry's law, according to which the equilibrium concentration of air dissolved in PDMS is directly proportional to the partial pressure of the air around the PDMS as

$$c = s \cdot p, \quad (1)$$

where c is the concentration of air molecules in PDMS, S is the solubility coefficient of air in PDMS, and p is the pressure of air.

When a PDMS slab is placed in a vacuum environment, the air dissolved in PDMS is evacuated owing to its poor solubility at low pressure and a low-pressure dissolution equilibrium is established. After it is brought back to the atmosphere, the original equilibrium is disturbed, and air is re-dissolved into the surface layer of the PDMS matrix and then diffused into its interior until a new equilibrium is reached. In terms of solubility, the amount of air transported into PDMS, Δm , can be written as

$$\Delta m = (c_{\text{atm}} - c_0)V_{\text{PDMS}} = S(p_{\text{atm}} - p_0)V_{\text{PDMS}}, \quad (2)$$

where c_{atm} and c_0 are the equilibrium concentrations of air in PDMS at atmosphere and vacuum environment, respectively; p_{atm} and p_0 are the air pressures around PDMS at atmosphere and vacuum environment, respectively; and V_{PDMS} is the volume of the PDMS slab. This equation indicates that the amount of air transferred into PDMS depends on both the size of the PDMS slab and the vacuum level at the degassing step. In terms of diffusion, the amount of air transported into PDMS can be written as

$$\Delta m = \oint_A \mathbf{J} \cdot \mathbf{n} dS, \quad (3)$$

where $\mathbf{J}$ is the mass flux through per unit area, $\mathbf{n}$ is the unit normal vector, and A is the total surface area exposed to air. Since the transportation of air occurs on all faces of the PDMS slab, in order to better describe the relationship between the geometry and the characteristics of the degassed PDMS pump, the mass transport is divided into two parts: one is transferred through the surface exposed to the outside environment and the other is transferred through the surface exposed to the closed system. Thus, Eq. (3) can be rewritten as

$$\Delta m = \Delta m_1 + \Delta m_2 = \oint_{A_1} \mathbf{J}_1 \cdot \mathbf{n} dS + \oint_{A_2} \mathbf{J}_2 \cdot \mathbf{n} dS, \quad (4)$$

where Δm_1 and Δm_2 represent the amount of air transported into PDMS through the surface areas exposed to the closed system and the outside environment, respectively; $\mathbf{J}_1$ and $\mathbf{J}_2$ are the mass fluxes through per unit area exposed to the closed system and the outside environment, respectively; and A_1 and A_2 are the surface areas exposed to the closed system and the outside environment, respectively. By assuming that both of $\mathbf{J}_1$ and $\mathbf{J}_2$ are uniform and everywhere normal to the surface area of PDMS, they can be taken out of the integral. Thus, we then have

$$\Delta m = \Delta m_1 + \Delta m_2 = A_1 \mathbf{J}_1 + A_2 \mathbf{J}_2. \quad (5)$$

For a given degas-driven PDMS pump, the amount of air dissolved in it is fixed. However, only the absorption of air occurs within the closed system, $A_1 \mathbf{J}_1$, makes a positive contribution to pumping pressure; therefore, it can be deduced that the surface area exposed to the outside environment, A_2 , also affects the performance of the PDMS pump. According to the ideal air law, the pressure in a closed microfluidic system can be expressed as

$$P = \frac{mRT}{MV}, \quad (6)$$

where p is the pressure of air, m is the mass of air in the closed system, M is the molar mass of air molecules, V is the volume of the closed system, and R and T represent the air constant and absolute temperature, respectively. By assuming that volume V and temperature T are kept constant, the pressure is directly proportional to the amount of air confined in the closed system. When the air in the closed system is dissolved in the degassed PDMS, the pressure will

fall in response to the change in the amount of air. By combining Eqs. (5) and (6), the change of pressure, Δp , can be written as

$$\Delta p = \frac{\Delta m_1 RT}{MV} = \frac{A_1 RT}{MV} \mathbf{J}_1. \quad (7)$$

The mass flux $\mathbf{J}_1$ is assumed to obey Fick's first law

$$\mathbf{J}_1 = -D \nabla c, \quad (8)$$

where D is the diffusion coefficient, and ∇c denotes the concentration gradient. Substituting Eq. (8) into Eq. (7) gives

$$\Delta p = \frac{A_1 D R T}{M V} \nabla c. \quad (9)$$

For the degas-driven PDMS pump, Δp can be regarded as the difference between the internal and external air pressures of the closed system, which serves as the driving force of the pump. Thus, Eq. (9) reveals that the pumping activity of the pump depends on diffusion area A_1 , system volume V , and concentration gradient ∇c .

III. EXPERIMENTAL SECTION

A. Design and fabrication of micropump

The proposed modular PDMS pump is composed of a PDMS slab containing one or multiple chambers with an array of micro-posts that are designed to increase the diffusion area. Each chamber acts as a pump module. To determine the effects of various devices and experimental parameters on the activity of pumping, several pumps of different geometries were fabricated. All pumps and microfluidic devices used in the experiments were created by utilizing the well-established soft lithography techniques.⁴⁰ Briefly, a master was prepared from a negative photoresist, SU-8 (Microchem, USA). Subsequently, the PDMS prepolymer (Sylgard 184, Dow Corning) was prepared by mixing the PDMS base and curing-agent and poured over the master. In all experiments except for investigating the effect of PDMS cross-linking degree, the mixing ratio of base to curing-agent was 10:1 (w/w). After curing, the PDMS slab was peeled off from the master, and the pump modules were cut out using a scalpel.

B. Operation of micropump

A basic operational schematic for the modular PDMS pump is shown in Fig. 1. To activate the PDMS pump, the pump slab was placed in a vacuum desiccator and degassed at 10 kPa overnight (Fig. 1(a)). Subsequently, the degassed PDMS slab was taken out from the vacuum chamber and placed directly onto the outlet port of a microfluidic device (Fig. 1(b)). It must be noted that the chamber of the pump slab needs to be aligned with the outlet port opening of the microchip prior to placing. As for a pump configuration with multiple chambers, each module must be aligned with the corresponding outlet prior to placing. Owing to the natural compliance and adhesion of PDMS, the pump slab conforms efficiently to the topography of microchip to form a leak-free seal. To ensure a reliable sealing, the user can manually press the PDMS slab after placing. After that, aliquots of liquid samples were loaded onto the inlet ports using a conventional micropipette (Fig. 1(c)). Under the negative pressure created by the degassed PDMS pump, the samples were sucked into the microchip (Fig. 1(d)). In the case of a procedure requiring a long time or multistep microfluidic control, the pump slab can be simply peeled off from the microchip and replaced with another degassed PDMS slab.

C. Characterization of micropump

The most important and basic parameter associated with the pump is the pumping pressure; therefore, a measurement of the pumping pressure was done rather than the flow rate that is

generally investigated in micropump studies. The experimental setup for the pumping pressure measurements is illustrated in Fig. 2. A vertically positioned Teflon tube with one end connected to a PDMS socket containing a venting port was used for measuring the pumping pressure. The tube was 500 μm in inner diameter and 12.2 cm in length. The thickness of the socket was 4 mm, and the diameter of the venting port was 0.75 mm. Food dye solution (1%, w/v) (Shanghai Jiahui Fine Chemicals Co., Ltd) was served as the pumping fluid for direct optical visibility. During the pumping pressure measurement, a modular PDMS pump was adhered to the surface of the socket with its pump chamber in alignment with the venting hole, and then, the other end of the tube was vertically immersed into a Petri dish filled with food dye solution. Owing to the large opening of the Petri dish, the liquid level change in the Petri dish during the pumping process is negligible. For all experiments, the idle time was 3 min, which was

FIG. 2. Schematic drawing of the experimental setup for measuring the pumping pressure.

defined as the interval between the time when the PDMS pump is taken out from vacuum and the time when liquid blocks the inlets of the tube or the microfluidic devices equipped with the PDMS pump. Once the bottom end of the tube was immersed into food dye solution, the images were captured at an interval of 1 min using the CCD camera until the movement of the liquid front stopped. The pumping pressure was evaluated by monitoring the elevation of the liquid column in the tube.

In addition to measuring the pumping pressure, we also investigated the induction time of flow driven by the PDMS pump. In the induction time measurement, the pump/microchip assembly was horizontally mounted on the stage of an inverted microscope (IX-51, Olympus, Japan) equipped with a CCD camera (DP70, Olympus, Japan), and a drop of food dye solution was added to the inlet of the microchannel by a micropipette. When the inlet was blocked, the images were captured at an interval of 1 s using the CCD camera. The induction time of flow related to the PDMS pump is defined as the interval between the time when the liquid is loaded onto the inlet and the time when the liquid front enters the microchannel.

D. Crystallization experiments

To demonstrate applicability to a common microfluidic task, the modular PDMS pump was combined with a specific designed microfluidic device for precisely metering and mixing the protein and the precipitant solutions for the protein crystallization test. For the crystallization experiments reported in this study, lysozyme was used as the model protein for investigating the application of the pump in protein crystallization. The concentration of lysozyme was 40 mg/ml in 0.1 M sodium acetate buffer with pH 4.6 and the precipitating agent was 1.0 M NaCl/0.1 M NaAc pH 4.8/25% ethylene glycol. Subsequent to metering and mixing the protein and the precipitant solutions in the microfluidic device by using the PDMS pump, the device was preserved in a refrigerator at 4 °C for 24 h. After 24 h, the chamber was examined by an inverted microscope (IX-51, Olympus, Japan). Optical micrographs were obtained using a CCD camera (DP70, Olympus, Japan).

IV. RESULTS AND DISCUSSION

A. Measurements of pumping pressure and induction time

As shown in Fig. 2, the kinetics of the pumping pressure was measured by monitoring the liquid level change in a Teflon tube when the PDMS pump slab was placed onto the socket connected with the tube. In this experimental setup, there are three contributions to the pumping pressure Δp : static fluid pressure p_s , capillary pressure p_c , and dynamic pressure p_d ; and $\Delta p = p_s + p_c + p_d$ (as shown Fig. 3). Δp is the difference between the internal and external air pressure, i.e., $\Delta p = p_o - p_i$, where p_o is the atmosphere pressure and p_i is the air pressure inside the tube; p_s is the pressure contributed by the potential energy of the fluid in the tube, i.e., $p_s = \rho gh$, where g is the acceleration of gravity, and h is the height of the liquid column in the tube; p_c is the pressure contributed by capillary force, i.e., $p_c = 2\gamma \cos \theta / r$, where γ is the surface tension of the fluid, θ is the dynamic contact angle of the fluid with the Teflon tube, and r is the inner radius of the tube; p_d is the pressure contributed by the kinetic energy of the fluid in the tube, i.e., $p_d = \rho v^2 / 2$, where ρ is the density of the fluid, and v is the velocity of the fluid. In our experiment, a typical velocity of flow, v , is less than 0.1 mm/s, relating to a dynamic pressure in the order of 10^{-6} Pa, which is far less than both the static fluid pressure (in the order of 10–100 Pa) and the capillary pressure (about 70 Pa with surface tension of 63 mN/m, dynamic contact angle of 98°, and inner diameter of 0.5 mm). Thus, the contribution of p_d is negligible in the calculation of Δp , and the pumping pressure is simply calculated by adding the static fluid pressure to the capillary pressure.

In most cases, an operated microfluidic device is horizontally placed. For this system, the pumping pressure provided by the PDMS pump can be only divided into two parts: capillary pressure and dynamic pressure, i.e., $\Delta p = p_c + p_d$. For commonly used PDMS-based microfluidic devices whose surfaces are generally not wettable by aqueous solutions, $p_c \geq 0$, it is

FIG. 3. Pressures in the degassed PDMS manometer. p_o is the atmosphere pressure; p_i is the air pressure inside the teflon tube; p_c is the pressure caused by capillary force; h is the height of the liquid column inside the tube; and θ is the dynamic contact angle of the fluid with the teflon tube.

required for the beginning of flow in PDMS devices that the pumping pressure exceeds the pressure barrier yielded by the capillary effect, i.e., $\Delta p \geq p_c$. Owing to the dynamic process of the diffusion of air into PDMS from the closed channel, the internal pressure p_i gradually decreases with time; accordingly, the pumping pressure, $\Delta p = p_o - p_i$, gradually increases with time. Thus, there is a delay interval between the time the PDMS pump is mounted on a PDMS microfluidic device and the onset of flow in it. This interval, which we define as the induction time of flow, is a key parameter that affects fluid manipulation within a microfluidic system. Apart from the geometry and surface characteristics of channel, the induction time of flow in a microfluidic device depends on the performance of the PDMS pump mounted. To investigate the effect of pump chamber surface area on the induction time of flow, a PDMS device was designed with six independent equal-length channels. One end of each channel was connected to a common inlet port, and the other end was sealed with a PDMS pump module (shown in pink color) in varying pump chamber surface area: 15.5, 30.4, 45.3, 60.2, 75.1, and 90.0 mm², as shown in Fig. 4(a). Note that the surface area of pump module can be adjusted by altering the size of pump chamber and the number or density of micro-posts contained in the pump chamber. For the PDMS device used here, the channel dimensions were 15 μ m height and 100 μ m width, and the outlet port was 1 mm in diameter. In addition, for investigating the effect of the initial volume of the closed system on the induction time of flow, the above device was modified by changing the size of outlet ports with variable diameters of 4.0, 3.5, 2.5, 1.5, 0.75, and 0.25 mm, and a group of pump modules with the same size pump chamber (53.5 mm² in surface area) were mounted on these outlet ports (as shown in Fig. 4(b)).

B. Effect of pump chamber surface area

The pumping performance of a degas-based PDMS pump is mainly dependent on the solution-diffusion process of air in a closed microfluidic system. Since gas molecules need to come in contact with the degassed PDMS to dissolve, the amount of surface area available for the dissolving gas molecules is a key parameter that affects the performance of the degas-based PDMS pump. The effect of surface area was investigated by measuring the pumping pressures

FIG. 4. Schematic drawing of the devices for investigating (a) the effect of the pump chamber surface area on the induction time of flow triggered by the modular PDMS pump, and (b) the effect of the initial volume of the closed system on the induction time of flow triggered by the modular PDMS pump.

of different pumps with the chamber geometries of varying surface areas: 15.5, 30.4, 45.3, 60.2, 75.1, and 90.0 mm². The effective surface area of the pump includes the surface of the pump chamber side wall and ceiling and that of micro-posts contained in the pump chamber. All PDMS pump slabs were 22 mm in length, 7 mm in width, and 4 mm in height. Fig. 5 shows the experimental measurements of the pumping pressure *versus* time at various surface areas. As predicted in Eq. (9), the pumping pressure increases with the increase of the surface area of the pump chamber. Besides, it can be clearly seen from Fig. 5(a) that the pumping pressure increases linearly in the first 15 min for all conditions. The larger the surface area is, the faster the pumping pressure increases. This effect was further demonstrated by the measurements of induction time of flow (Fig. 5(b)). A larger diffusion area causes a shorter induction time. Thus, it is possible to find optimum combination of the pump modules for performing operations in a pre-programmed sequence by adjusting the surface area of the pump chamber. In addition, as a larger diffusion area results in more mass being transported into the PDMS matrix and then a faster rate to establish the equilibrium, the duration time of the pumping activity, defined as the period between the mounting of the pump and the stop of flow, decreases with the increase of the surface area of the pump.

C. Effect of system volume

The initial volume of the closed system is another factor that affects the pumping performance. According to Eq. (9), for a given pump, i.e., diffusion area A_1 and concentration gradient ∇c is constant in Eq. (9), the pumping pressure Δp is inversely proportional to the system volume V . To investigate the effect of changing the initial volume of the system on the pumping pressure, the device shown in Fig. 2 was modified by adding a through-hole PDMS interconnect between the PDMS pump and the socket. By changing the diameter of the through-hole in the PDMS interconnect, the volume of the system can be adjusted while maintaining all other factors constant. In our experiment, three initial system volumes (25.7 mm³, 55.1 mm³, and 75.4 mm³) were tested using the PDMS pump with the chamber surface area of 53.5 mm² and the size of 12 mm (L)×12 mm (W)×4 mm (H). Fig. 6(a) presents the pumping pressure *versus* the system volumes. As expected, the pumping pressure decreases with the increase of the system volume. This tendency was confirmed by the measurements of induction time. It can be clearly seen from Fig. 6(b) that the bigger the system volume is, the more time is required for the onset of flow in the microfluidic device.

FIG. 5. Effect of the effective surface area of the pump chamber on the pumping pressure generated by the modular PDMS pump. (a) Plot of pumping pressure generated by the modular PDMS pumps with varying surface area vs time, and (b) plot of the induction time of flow triggered by the different modular PDMS pumps with varying surface area.

D. Effect of exposure area

The third aspect that affects pumping performance is the exposure area of the pumping. As mentioned previously, in respect of the contribution to pumping, the air absorbed into the PDMS pump bulk could be divided into two parts, inside and outside of the closed system. Although only the air absorption inside the closed system contributes to the generation of pumping pressure, the air absorption through the outside surface of the degassed PDMS pump increases the concentration of air in the PDMS bulk, which decreases the rate and amount of the air absorption through the inside surface area of the PDMS pump, and thus affects the performance of the PDMS pump. To investigate the effect of the PDMS pump exposure area on its performance, three cases of PDMS pump exposure area (100%, 70%, and 0%) were compared using the PDMS pump with the chamber surface area of 15.5 mm² and the size of

FIG. 6. Effect of the initial volume of the closed system on the pumping pressure generated by the modular PDMS pump. (a) Plot of pumping pressure generated in the closed systems with varying volume vs time, and (b) plot of the induction time of flow by a modular PDMS pump in the closed systems with varying volume.

7 mm (L) $\times$ 7 mm (W) $\times$ 4 mm (H). The exposure ratio is defined as the ratio between the outside surface area of the PDMS pump in contact with air and the entire outside surface area of the PDMS pump. A PDMS pump exposure area of 70% was achieved by coating a layer of epoxy glue on the top of the PDMS pump slab, while a PDMS exposure area of 0% was achieved by sealing the entire outside surface of the PDMS pump slab with epoxy glue, leaving only the contact face unsealed (as shown in Figs. 7(a)–7(c). Fig. 7(d) shows a summary of the measurement results of the pumping pressure *versus* the exposure area of pumps. It can be seen that as the exposure ratio of the degassed PDMS pump increases, the acceleration rate and maximum magnitude of the pumping pressure decreases and the duration time of pumping also decreases. Thus, it is obvious that minimizing the exposure surface area of the degassed PDMS pump is important for this pumping method to achieve a higher driving pressure and maintain a longer working time. These results are different from those reported previously by Liang *et al.*,⁴¹ in which it was thought that PDMS exposure area did not considerably impact the degas-driven

FIG. 7. Effect of the exposure area of the pump slab on the pumping pressure. (a)–(c) Side-view schematic drawing of the three conditions that were tested: 100% exposure with the entire non-contact surface of the pump being exposed to atmosphere, 70% exposure with the top of the pump being coated by a layer of epoxy glue, and 0% exposure with the entire non-contact surface of the pump being coated by a layer of epoxy glue. (d) Plot of pumping pressure generated by the modular PDMS pumps with varying exposure area vs time.

flow dynamics. There are several reasons why our results might contradict their conclusions. First, the ratio of the inside surface area of the degassed pump to the initial volume of the closed system in their experimental setup is far higher than that in this study; therefore, for their experimental setup, the rate of inner air absorption is faster than that of the outer in their system so that the amount of dissolved air in the inner surface of the closed system nearly arrives at equilibrium concentration before the outer air absorption obviously increases the concentration of air in PDMS. Furthermore, the sealing strategies are different among the two studies. In their study, the degassed PDMS devices were immersed in silicone oil to block the outer air absorption. As a certain amount of air is dissolved into liquid, it is hard to completely prevent the outer air absorption for the degassed PDMS with this sealing method.

E. Effect of pump slab volume

According to Eq. (2), the size of the PDMS pump slab plays an important role in determining the amount of air absorption into the PDMS slab and thus affects the performance of the degassed PDMS pump. To investigate the effect of PDMS pump volume on its performance, two PDMS pumps with respective volume of 196 mm^3 and 400 mm^3 were compared. The effective surface area of the pump chamber and the exposure ratios of the pump surface area were similar for both pumps, 15.5 mm^2 and 0%, respectively. Fig. 8 shows the effect of the PDMS pump volume on its pumping capacity. As a larger PDMS pump dissolves more air into it, and needs more time for air diffusion owing to a longer diffusion path, the acceleration rate

FIG. 8. Effect of the pump slab volume on the pumping pressure.

and maximum magnitude of the pumping pressure, as well as the duration time of pumping, increases with the increase of the PDMS pump volume. Based on the experiment results, it can be mentioned that a pump with a volume of 400 mm^3 can maintain its pumping activity for more than 8 h. To the best of our knowledge, this duration time of pumping activity is far longer than that provided by the existing degas-driven pumps. A long duration of pumping activity may be useful for many microfluidic systems, for example, cell culture chips, which generally require a long period and continuous liquid nutrient feeding.

F. Effect of PDMS cross-linking degree

To investigate the effect of PDMS cross-linking degree on the performance of PDMS pump, three PDMS pumps were prepared by mixing the PDMS base and curing-agent at 5:1 (w/w), 10:1 (w/w), and 20:1 (w/w), respectively. Except the ratio of pre-polymer to cross-linker, all other parameters of three PDMS pumps were kept the same, including the effective surface area of the pump chamber (15.5 mm^2), the system initial volume (25.7 mm^3), the pump slab volume (400 mm^3), and the exposure ratios of the pump surface area (72%). As shown in Fig. 9, the lower

FIG. 9. Effect of pre-polymer/cross-linker ratio on the pumping pressure of PDMS pump.

FIG. 10. (a) Vacuum-sealed PDMS pump. (b) Application of the modular PDMS pump to glass microfluidic device: one drop of colored fluid is transported from the inlet port to the outlet port by the action of the modular PDMS pump, while the other remains stationary without applying a PDMS pump.

the amount of cross-linker, the higher the pumping pressure of PDMS pump. Such behaviour can be explained by the increase in the fractional free volume of PDMS with the decrease of the PDMS cross-linking degree. As the dissolved amount and the diffusion rate of air in PDMS matrix are positively correlated to the fractional free volume of PDMS, the acceleration rate and maximum magnitude of the pumping pressure increases with the decrease of PDMS cross-linking degree. However, the pumping pressures generated by the 10:1 PDMS pump and the 5:1 PDMS pump show only a small difference. It may be because there is nearly the same cross-linking degree for the 10:1 PDMS pump and the 5:1 PDMS pump.

G. Application

For the user's convenience, the modular degassed PDMS pump can be prepared by producer and be stored in an air-tight packaging (as shown in Fig. 10(a)). In practical applications, a user is only required to open the package, take out the pre-degassed PDMS pump slab, and place it on the outlet ports of a microfluidic device. This modular design of the degas-based PDMS pump not only provides convenience for user but also expands the application range of the degas-based pump from PDMS-based microfluidic devices to other material microfluidic devices. As shown in Figure 10(b), a pre-degassed modular PDMS pump was mounted on a glass microfluidic chip and was used to move a drop of liquid down a microchannel. The glass chip used consisted of two independent parallel microchannels ($40\ \mu\text{m}$ in width and $10\ \mu\text{m}$ in depth), each being connected to an inlet port and an outlet port. First, the outlet port of the upper left microchannel was sealed with a pre-degassed modular PDMS pump, while the outlet port of the other microchannel kept opening. Then, two drops (each $8\ \mu\text{l}$) of dye solution were dispensed into two inlet ports, respectively. After dispensing, the liquid was spontaneously drawn into the channels by capillary action and stopped at the end of channels by capillary pressure barriers.⁴² For the lower right channel, since no additional pressure was applied, the liquid in it remained stationary (only a little evaporation loss). For the upper left channel, however, the liquid in it continuously flowed due to a driven pressure provided by the PDMS pump, and a droplet ($8\ \mu\text{l}$) in the inlet port was transported to the outlet port after 30 min (as shown in Fig. 10(b)). The above experiment result shows that the modular PDMS pumping method is universal to microfluidic devices. It only requires a flat and smooth surface around the outlet port of microfluidic device for mounting PDMS pump. Owing to the natural compliance and adhesion of PDMS, the pump slab mounted is apt to conform to the topography of microchip and form a leak-free seal, which is necessary for the degassed PDMS pump to generate negative pressure for pumping fluid.

To further demonstrate a potential application for such a modular PDMS pump, a PDMS pump containing three modules was combined with a specifically designed microfluidic device for protein crystallization test. Fig. 11 presents the schematic diagram of microdevices used in this study. The protein crystallization chip made of PDMS consisted of three-dimensional microchannel networks, in which nanoliter-sized liquids could automatically and accurately be metered and mixed by combining the capillary stop valve with the negative pressure generated

FIG. 11. Schematic drawing of the pump/microchip assembly device for testing protein crystallization.

by the degassed PDMS pump. It can be seen from Fig. 11 that two shallow channels connect two liquid metering channels to a mixing channel. Meanwhile, a row of shallower channels connect the reaction chamber to a venting channel. The shallow channels with depths typically ranging from 5 to 15 μm functioned as capillary stop valves.⁴² Liquid operations in this device were performed by employing the dynamic pressure generated by the degassed PDMS pump. First, a degassed PDMS pump was placed onto the protein crystallization chip, allowing its three pump chambers to be aligned with the three outlet ports, respectively. Then, liquid A and liquid B of 0.5 μl volume were loaded into two inlet ports, respectively. Under the action of a negative pressure created inside the microchannel by the air absorption of the degassed PDMS pump, liquids were introduced to the feeding channels and metering channels. At this moment, it was observed that the liquids stopped at the entrance of the capillary valves as a larger reverse capillary pressures existed at these narrow channels. Subsequently, air was introduced to remove the excess liquid in the feeding channels, and droplets of precise volumes were left in the metering channels. Owing to the continuous diffusion of air into the PDMS pump bulk, the negative pressure in the mixing microchannel further increased, which caused two droplets to overcome the capillary barrier and enter the mixing channel. It was observed that the two

FIG. 12. A sequence of close-up photographs of liquid metering and mixing in the pump/microchip assembly device. (a) and (b) introduction of dye solution, (c) and (d) metering of dye solution by introducing air from the inlet, (e) injection and mixing of dye solution, and (f) transport of mixed liquid to the reaction chamber.

FIG. 13. Lysozyme crystal formed in microdevice.

droplets coalesced and mixed immediately after entering the mixing channel. Next, the mixed droplet was pushed into the reaction chamber for subsequent detection and analysis. Fig. 12 shows snapshots of the dispensing and mixing of two food dye solutions. Finally, lysozyme crystallization was tested using this assembly device. As shown in Fig. 13, a crystal of lysozyme of dimension up to $100\text{ }\mu\text{m} \times 160\text{ }\mu\text{m}$ was produced in the microdevice, which successfully demonstrated the practical value of the modular PDMS pump.

V. CONCLUSION

In this paper, we present a modular pump that exploits the air absorption behavior of the degassed PDMS bulk to create a negative pressure for fluid manipulation in microfluidic devices. Different from monolithic degassed PDMS pumps in several existing microfluidic systems, the modular degassed PDMS pump can be easily removed and replaced, which significantly increases the flexibility and application range of microfluidic systems, meanwhile reducing the complexity and cost of microfluidic devices. In addition, the effects of several key parameters on the performance of the degassed PDMS pump were also systematically investigated. These parameters include the effective surface area of the pump chamber, the initial volume of the microfluidic system, the exposure area, the volume of the PDMS pump, and the cross-linking degree of PDMS. The experimental results demonstrate that it is possible to flexibly build microfluidic systems for achieving the desired flow control in a given application by mounting the modular pumps with a specific combination of the above-mentioned parameters. It is believed that this modular pumping concept might find extensive use in lab-on-a-chip devices, particularly in disposable cartridges for point-of-care diagnostic tests.

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