

Reversible lossless manipulation of water droplets with large-range volume

Liu Huang^{1,2}, Xuyue Wang¹, Changlin Zhao^{1,2}, Jiyu Liu^{1,2}, Ziai Liu^{1,2}, Yankui Sun^{1,2}, Xin Liu^{1,2}, Jinlong Song^{1,2} ✉

¹Key Laboratory for Precision and Non-Traditional Machining Technology of the Ministry of Education, Dalian University of Technology, Dalian 116024, People's Republic of China

²Collaborative Innovation Center of Major Machine Manufacturing in Liaoning, Dalian University of Technology, Dalian 116024, People's Republic of China

✉ E-mail: songjinlong@dlut.edu.cn

Published in Micro & Nano Letters; Received on 7th November 2017; Revised on 25th February 2018; Accepted on 9th March 2018

The lossless manipulation of microdroplets has great promising applications in the fields of such as liquids transportation. In recent years, superhydrophobic surfaces with low adhesion have been utilised as an effective solid surface to realise the lossless transfer of liquids. However, the present methods using superhydrophobic surfaces are hard to realise the reversible lossless manipulation of water droplets with a large-range volume. Here, a special transfer pipette composed of a superhydrophobic hole and an optimised pressure-generation device is developed to realise the lossless manipulation of water droplets. The superhydrophobic surfaces are obtained by electrochemical etching, boiling-water immersion and stearic acid modification, showing an excellent superhydrophobicity with a water contact angle of $\sim 165^\circ$ and roll-off angle of $\sim 2^\circ$. The capture and release of water droplets are realised via controlling the resultant force of the vertical component of capillary force and gravity of droplets. The applied pressure is far less than the threshold pressure which guarantees the lossless property in the manipulation processes. The operable limiting volume of water droplets even reaches to 1404 μL , showing a large-range operable volume. Moreover, the strategy can easily realise the reversible and repeatable manipulation showing potential applications in the biological and microfluidic fields.

1. Introduction: The lossless manipulation of droplets has attracted much attention, which shows a big potential application prospect in the fields such as microfluidic devices [1–5], biochemical separation [6, 7], and micro-reaction system [8–10]. Currently, artificial superhydrophobic surfaces with water contact angles (CAs) larger than 150° have been widely investigated in the lossless manipulation because of their water-non-sticky property [11]. The present methods using superhydrophobic surfaces to manipulate droplets can be divided into two types: non-in-situ control and in-situ control. Non-in-situ control often uses gecko feet/rose petal/mussel-inspired superhydrophobic surfaces to manipulate droplets [12–22]. These surfaces are also called high adhesive superhydrophobic surfaces which allow water droplets to adhere to the surfaces even when the surfaces are turned upside down but still with water CAs larger than 150° . However, the reversibility of non-in-situ control method is poorly operated. This method can only transfer the droplet from superhydrophobic surfaces to other hydrophobic/hydrophilic/superhydrophilic surfaces with no loss for one time and cannot transfer the droplet to non-sticky surfaces for several times. As for in-situ control, extra applied energy, such as UV irradiation [23], electrical potential [24], temperature [25], pH [25], magnetic field [26], gas [27], density [28], and deformation [29], are used as driving force to realise the in-situ switching between pinned and roll-down superhydrophobic states and to further undergo the in-situ capture and release of droplets. However, the aforementioned driving methods in the in-situ control are harsh and not suitable for mild condition applications.

In addition, the immediate driving force in the non-in-situ control and in-situ control is mainly the solid-liquid adhesive force. Since the adhesive force is very small and no more than 100 μN , the operable volume of droplets in the manipulation process is just severely limited. Specially, the magnetic field driven in-situ control uses magnetic force as the capture force, while can only control the magnetic droplet. So finding an intelligent method for the in-situ lossless manipulation of water droplets with a large-range operable volume in air has been greatly needed.

In a previous study, the underwater lossless manipulation of non-polar organic liquids was easily realised based on a designed transfer pipette which was composed of a long-term underwater superoleophobic hole and a pressure-generation syringe [30]. The liquid droplets could be captured via supplying the suitable applied driving force, whereas removing the pressure could also make droplets released. Owing to the different media in air and underwater, once this method was applied to manipulating water droplets with no loss, the results would be difficult to be observed including operable volume range of droplets. Therefore, it is necessary to actualise the lossless manipulation of water droplets for the sake of integrating this manipulation mechanism. Here, the transfer pipette is composed of a superhydrophobic hole and optimised pressure-generation device where a micro syringe pump replaces the manual operation. In addition, the superhydrophobic surfaces on Al substrates are prepared by the electrochemical etching and boiling-water immersion followed by stearic acid (STA) modification. Additionally, an intelligent mechanical hand for lossless manipulation of water droplets is realised in air, which has a large operable range in volume. The operable limiting volume of water droplets is constant and reaches to 1404 μL , which is just determined by the CA, interface tension, and density of droplets.

2. Experimental

2.1. Materials: Aluminium (Al) rods (purity > 99%, 10 mm diameter, 20 mm length) and Al plates (purity > 99%, 30 mm $\times$ 40 mm $\times$ 2 mm) were purchased from the Dalian Aluminium Material Manufacturer (China). STA [$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$] was obtained from the Tianjin Damo Manufacturer (China). Analytical-grade NaCl and alcohol were obtained from Tianjin Kermel Chemical Reagent Manufacturer (China). In the experiment, water ($\gamma_{\text{lv}} = 72.1 \text{ mN/m}$) were dyed blue to aid visualisation and this almost did not change its surface tension.

2.2. Fabrication of superhydrophobic transfer pipette: Stepped hole (0.5 and 2 mm diameter, 5 and 15 mm depth, respectively) was drilled through the one end face of an Al rod. The end face with

0.5 mm hole was then polished mechanically using 800# and 1500# abrasive paper to remove the oxide layer and the impurities on the surface, ultrasonically cleaned with alcohol and deionised water. After drying, the treated end surface separated from the cathode Cu plate by a distance of 3 cm was electrochemical etched at 500 mA/cm² current density and 6 min processing time in the 0.1 mol/L NaCl electrolyte. Then, the electrochemically etched Al rod was immersed in the boiling water for 1 h and dried. After the formation of surface structures, the electrochemical etched and boiling-water immersed (EEBWI) Al surfaces were put into a 0.05 mol/L STA ethanol solution for 15 min to reduce the surface energy followed by 20 min heating at 100°C. Moreover, to characterise the superhydrophobic surfaces better, the plane Al plates were also treated by the aforementioned processes.

2.3. Properties of the transfer pipette: A micro-syringe pump with a syringe of 1 mL was connected with the as-prepared Al rod by installing a pressure soft tube into the 2 mm hole to prepare a transfer pipette. The syringe was used as a pressure-generation device to produce negative pressure in the hole of Al rod via pulling the syringe piston, which was driven by the micro-syringe pump. In the process of manipulating water droplets, the centrelines of the hole and water droplet should be in a straight line as much as possible.

2.4. Characterisation: The surface morphologies of the obtained samples were investigated using a scanning electron microscope (SEM, SUPRA 55 SAPHIRE, Germany). The surface chemical compositions were observed using an energy-dispersive X-ray spectroscopy (EDS, SUPRA 55 SAPHIRE, Germany), an X-ray diffractometer (XRD, Empyrean, Holland) and senior Fourier transform infrared spectrophotometer (FTIR, Thermo Fisher 6700, America). The CA and roll-off angle (RA) of the samples were measured using an optical CA meter (SL200KS, KINO, USA) at room temperature by dropping 5 μ L water droplets on samples. The RA was defined as the angle at which the liquid drop began to roll off on the gradually inclined surface.

3. Results and discussion

3.1. Wettability of the Al surfaces: Figs. 1a–c show the digital images of water droplets on the different Al surfaces, the insets are the CA images of water droplets on those surfaces. Fig. 1a shows that the electrochemical etched Al surface was superhydrophilic to water. After the boiling-water immersion, sample surfaces became dim and showed excellent superhydrophilicity towards water droplets with a fast spreading velocity when water droplets impinged on the EEBWI Al surface, as shown in Fig. 1b. Finally, after modification with STA, the character of the Al surfaces successfully changed from superhydrophilic to superhydrophobic with a water CA of $\sim 165^\circ$ (Fig. 1c). Fig. 1d shows that 15 μ L water droplets approached and detached from the prepared superhydrophobic Al surface at a velocity of 0.1 mm/s. The adhesion on the superhydrophobic Al surface was so low that the water droplet just left the surface and kept sticking to the needle. In addition, as shown in Fig. 1e, water droplets with a volume of 5 μ L could easily roll off from the $\sim 2^\circ$ inclined plane superhydrophobic sample showing an ultralow adhesion property.

Subsequently, the surface morphologies of the electrochemical etched Al surface, EEBWI Al surface and STA-modified EEBWI Al surface were observed in Fig. 2. Micrometre-scale rectangular-shaped pits and bosses with size between 1 and 5 μ m which seemed like a maze [31] were formed on the Al surfaces via the electrochemical etching, as shown in Fig. 2a. After boiling-water immersion, such surfaces were covered with one layer of nanometre-scale needle-like structures, as shown in Fig. 2b. In contrast to the STA-modified EEBWI Al surface (Fig. 2c), there was

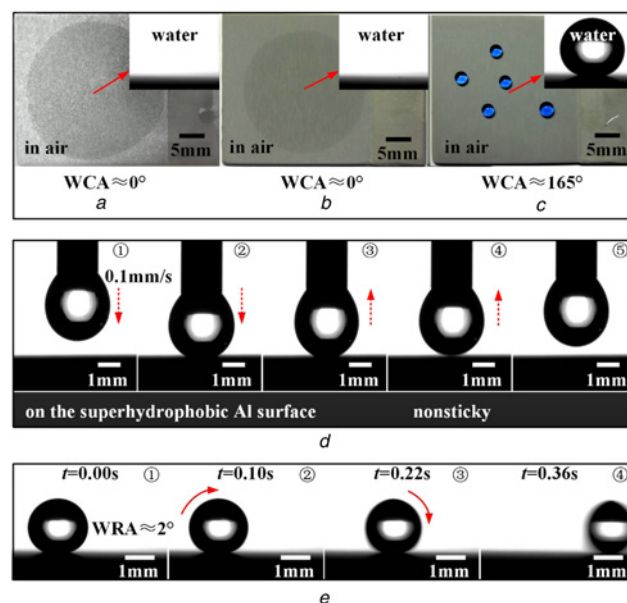


Fig. 1 Digital images of water droplets on
a Electrochemical etched Al surface
b EEBWI Al surface
c STA-modified EEBWI Al surface
d Experimental optical images of placing a 15 μ L water droplet on the STA-modified EEBWI Al surface
e Time-lapsed snapshots of water droplets rolling on an inclined STA-modified EEBWI Al surface

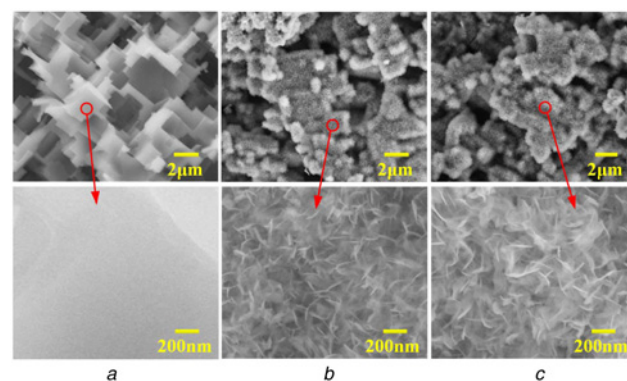


Fig. 2 SEM images
a Electrochemical etched Al surface
b EEBWI Al surface and
c STA-modified EEBWI Al surface

almost no change in surface morphologies illustrating the little influence of STA on the surface structures.

The chemical compositions of the obtained samples were also observed using EDS spectra, XRD patterns and FTIR spectra. Figs. 3a–d show the EDS spectra of the Al surfaces under different processing conditions. After the boiling-water immersion, there was a significant increase in the amount of element O demonstrating the generation of Al oxide. Owing to the introduction of C-containing material, the amount of element C also increased from 3.78 to 17.15% in the modification process. The increase of C element is mainly contributed by the chemical absorption of low-energy groups like $-\text{CH}_2-$ chains [32–34], which results in the wettability transition from superhydrophilicity to superhydrophobicity. In order to further ascertain the detailed compositions of samples, the XRD patterns of the electrochemical etched Al surface and EEBWI Al surface were conducted in Fig. 3e. Compared with the electrochemical etched Al surface which just had diffraction

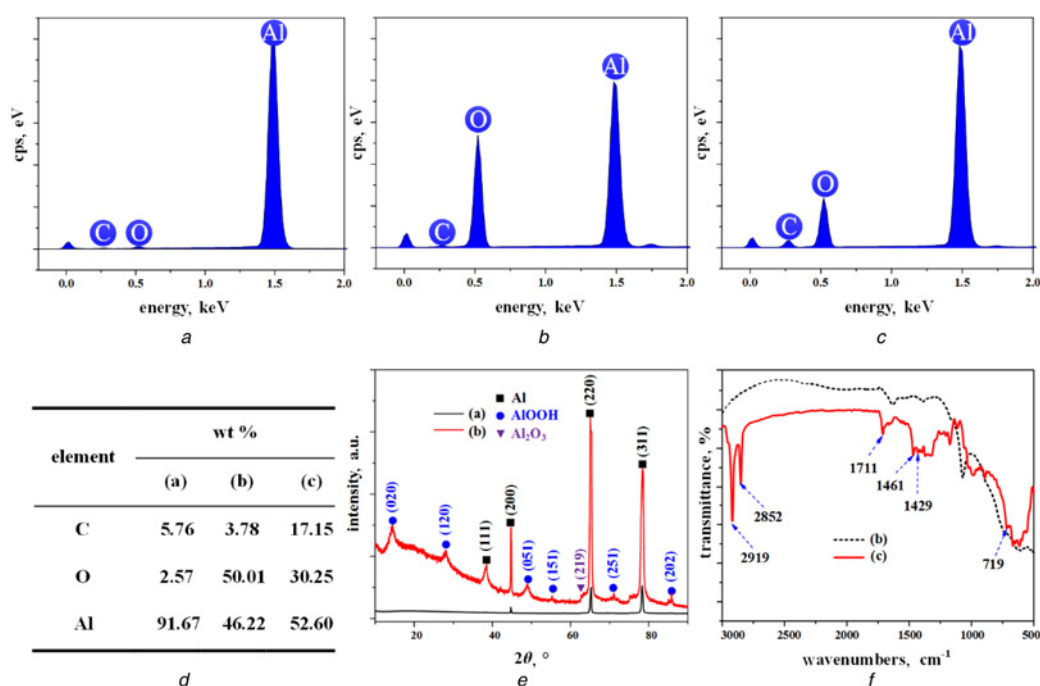


Fig. 3 Chemical compositions

a EDS spectra of electrochemical etched Al surface

b EDS spectra of EEBWI Al surface

c EDS spectra of STA-modified EEBWI Al surface

d Detailed amount of all the elements that those surfaces contained

e XRD patterns of the electrochemical etched Al surface before and after boiling-water immersion

f FTIR spectra of the EEBWI Al surface before and after STA modification

peaks of Al substrate, new diffraction peaks from AlOOH (JCPDS Card No. 21-1307) and Al_2O_3 (JCPDS Card No. 10-0414) were detected on the XRD pattern of EEBWI Al surface. Thus, the main compositions of the needle-like structures obtained by boiling-water immersion were AlOOH and Al_2O_3 . In addition, FTIR spectra were also applied to detecting the functional groups before and after STA modification, as shown in Fig. 3f. New peaks attributed to the C–H stretching vibrations of $-\text{CH}_2-$ groups were detected at the wave length of 2919 and 2852 cm^{-1} on the STA-modified samples [35–37]. The sharp absorptions at 719 , 1711 cm^{-1} , and $1429\text{--}1461\text{ cm}^{-1}$ were assigned to the O–H, C=O, and C–O stretching vibrations of the $-\text{COOH}$ group of STA molecules, respectively [35, 36]. Therefore, the self-assembled STA groups could effectively lower the surface energy, which resulted in the aforementioned wettability transition.

3.2. Lossless manipulation of water droplets: Figs. 4a and b show the schematic illustration of the designed transfer-pipette setup equipped with a micro syringe pump with a 1 mL syringe (pressure-generation device) and a prepared superhydrophobic hole on EEBWI Al rod. According to the morphologies of end surface and inner wall of hole, micrometre-scale maze-like structures were covered with nanometre-scale needle-like structures resulting in an excellent superhydrophobicity, as shown in Fig. 4c. The air pressure was regulated to capture the water droplets using the constructed transfer pipette, which was just an intelligent mechanical pulling movement. Thus, there was no water residues left on the transfer pipette or original superhydrophobic substrate, indicating the lossless property of manipulation processes. Additionally, there was no limit to the destination surface where the captured droplets can be released. Fig. 4d illustrates the complete lossless manipulation processes of water droplets. The transfer pipette first approached the target water droplet, captured the droplet under the certain pressure,

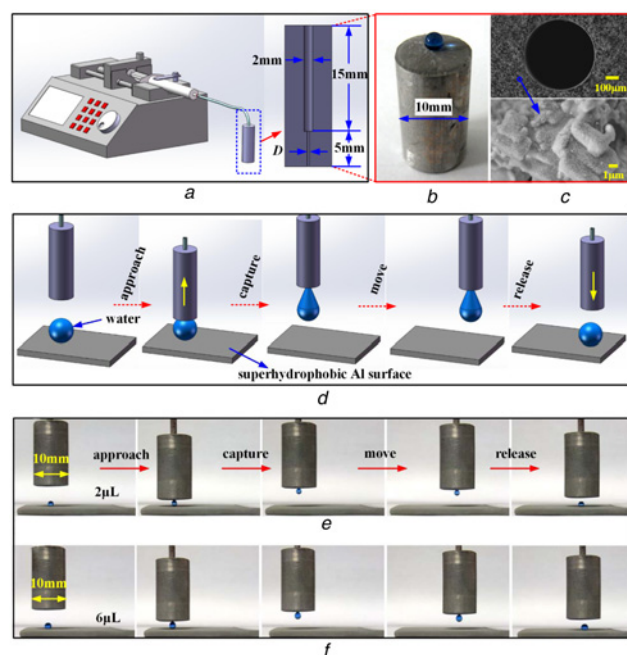


Fig. 4 Transfer equipment and processes

a Schematic illustration of the transfer-pipette setup

b and c Images of an equipped superhydrophobic hole on EEBWI Al rod

d Complete lossless manipulation processes of water droplets

e Detailed working process of losslessly manipulating $2\text{ }\mu\text{L}$ water droplet

f Detailed working process of losslessly manipulating $6\text{ }\mu\text{L}$ water droplet

then moved the droplet to the destination, and finally released the droplet after removing the applied pressure. Subsequently, the detailed and practical manipulation of water droplets were also

conducted, as shown in Figs. 4e and f. The water droplets of 2 and 6 μL were successfully controlled and manipulated to the destination without any residues.

3.3. Analysis of operable volume range: In general, the threshold pressure (P_t) can be defined as the pressure under which water droplets penetrate into the voids in the microstructures on the obtained superdophobic Al surfaces filled with air. For the purpose of realising the lossless manipulation, the applied pressure must be lower than the threshold pressure of water droplets. Thus, this threshold pressure P_t can be calculated as [38, 39]

$$P_t = \frac{4\gamma_w |\cos \theta|}{D_s} \quad (1)$$

where γ_w is the surface tension of water, θ is the CA of water droplet on the obtained superhydrophobic Al surfaces, and D_s is the spacing of the voids in the microstructures. Owing to the extremely low value of the spacing of the voids in the microstructures ($D_s \sim 5 \mu\text{m}$), the threshold pressure P_t is very large [31]. In our experiments, the values of γ_w and θ are 72.1 mN/m and 165° , respectively. So, $P_t = 55.7 \text{ kPa}$. The macro force analysis for a captured droplet in a balance state ($F_p = G$) is shown in Fig. 5a. In addition, $F_p = (\pi D^2 P/4)$ and $G = \rho_w V_w g$, where P is the applied pressure, G is the gravity of water droplet, D is the diameter of the superhydrophobic hole, V_w is the volume of water droplet, ρ_w is the density of water droplet and g is the acceleration due to gravity. So the applied pressure P can be given as follows:

$$P = \frac{4\rho_w V_w g}{\pi D^2} \quad (2)$$

For a 5 μL water droplet, the values of ρ_w , V_w , D , and g are 103 kg/m^3 , 5 μL , 0.5 mm, and 10 N/kg , respectively. Then, $P = 0.254 \text{ kPa}$. So, $P \ll P_t$, which guaranteed the feasibility of lossless manipulation.

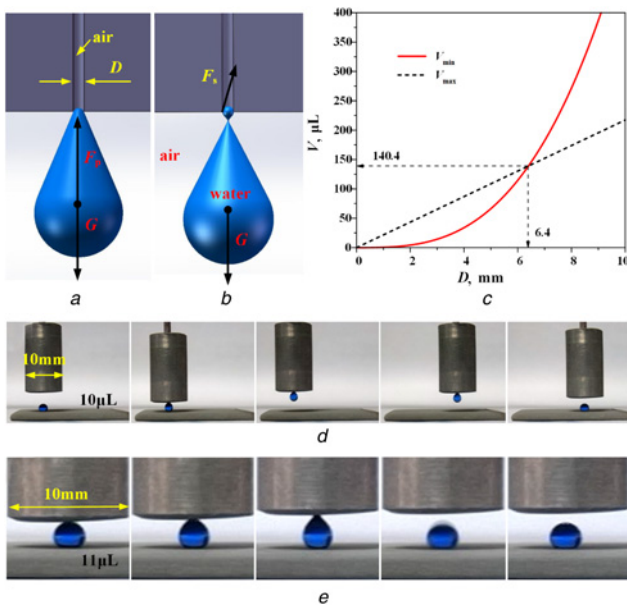


Fig. 5 Operable volume range

a Macro force analysis for a captured water droplet
b Breaking droplet from the hole because of the elastic deformation
c Change of the diameter of hole D on the operable volume of the droplet
d Practical manipulation processes of water droplet with a volume of 10 μL
e Practical manipulation processes of water droplet with a volume of 11 μL

Since the transfer pipette can freely realise the manipulation of water droplets via controlling the air pressure, the following work is just to investigate the operable volume range of the captured water droplet in an equilibrium. The minimum diameter of the water droplets should be larger than the size of the hole D and the minimum volume $V_{\min}$ is $(\pi D^3/6)$ which is similar with the underwater manipulation, while the maximum volume of the water droplets $V_{\max}$ just changes with the size of the hole D [30]. In the process of manipulating a water droplet with a large volume, the droplet will break for the elastic deformation which leads to a failed operation. So the droplet breaking mechanism should be explained theoretically. As shown in Fig. 5b, the dragging force is mainly provided by the vertical component of capillary force F_s between pending droplet and the superhydrophobic hole edge. The capillary force F_s is given by $F_s = \pi D \gamma_w$. By balancing the gravity of the pending droplet and capillary force, the operable maximum volume $V_{\max}$ can be predicted as

$$V_{\max} = \frac{\pi D \gamma_w |\cos \theta|}{\rho_w g} \quad (3)$$

From (3), we can find that $[\pi \gamma_w |\cos \theta| / (\rho_w g)]$ is constant, so the operable maximum volume of the droplet ($V_{\max}$) is in direct proportion to the diameter of the hole (D)

$$V_{\max} \propto D \quad (4)$$

Thus, the operable volume of water droplets ranges from $(\pi D^3/6)$ to $[\pi D \gamma_w |\cos \theta| / (\rho_w g)]$, and the detailed range is $(0.523 D^3, 21.73 D)$. For the hole of 0.5 mm, according to (4), the theoretical operable maximum volume $V_{\max}$ is about 10.86 μL . In our experiments (Figs. 5d and e), the transfer pipette with the hole of 0.5 mm could easily manipulate the water droplet of 10 μL , but could not capture the 11 μL droplet, showing that the theoretical results agree well with the experimental ones.

As a result of the detailed operable volume range, the change of the diameter of hole (D) on the operable volume ($V_{\min}$ and $V_{\max}$) is shown in Fig. 5c. In order to manipulate a droplet with a certain volume, what we need to do is just to choose a suitable diameter of the hole. Moreover, there is a limiting volume of the water droplet (V_{limit}) regardless of D which can be calculated by $V_{\min} = V_{\max}$, so is the corresponding limiting diameter of the hole (D_{limit}). Thus, they can be expressed as follows:

$$\begin{cases} V_{\text{limit}} = \frac{\pi}{6} \left(\frac{6\gamma_w |\cos \theta|}{\rho_w g} \right)^{3/2} \\ D_{\text{limit}} = \sqrt{\frac{6\gamma_w |\cos \theta|}{\rho_w g}} \end{cases} \quad (5)$$

For the experimental water droplet, we can obtain the result, $D_{\text{limit}} = 6.4 \text{ mm}$ and $V_{\text{limit}} = 140.4 \mu\text{L}$. Then, the calculated detailed results are shown in Table 1. Obviously, there is a large-range volume of water droplets for this manipulation process.

Table 1 Basic parameters of water droplets used in the experiments

Parameters	Water
γ_w , mN/m	72.1
θ , $^\circ$	165
$V_{\min}$, μL	$0.523 D^3$
$V_{\max}$, μL	$21.73 D$
D_{limit} , mm	6.4
V_{limit} , μL	140.4

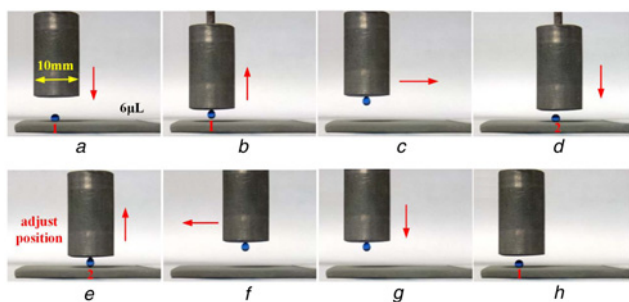


Fig. 6 Reversible and repeatable manipulation of the water droplet using the designed transfer pipette

3.4. Reversible and repeatable property of the manipulation processes: The reversible and repeatable property of this manipulating method was also observed by the designed transfer pipette, as shown in Fig. 6. The transfer pipette could easily capture one droplet, moving it from Position 1 to Position 2 followed by releasing it. Subsequently, the droplet was also reversibly captured and transferred to the original Position 1 after adjusting the position of the transfer pipette (since the released droplet slightly rolled to another position), which demonstrated the reversible and repeatable property of this manipulating method. Moreover, the prepared transferring device offers us a facile way to manipulate the water droplets precisely which can be potentially utilised to save the reactants and mix microdroplets with no loss.

4. Conclusion: In summary, STA was applied to modify the electrochemical etched and boiling-water immersed Al surfaces to obtain the superhydrophobicity. The prepared surfaces were covered with micrometre-scale rectangular-shaped pits and bosses, and nanometre-scale needle-like structures mainly containing AlOOH and Al_2O_3 , which showed a good superhydrophobicity with a water CA of $\sim 165^\circ$ and RA of $\sim 2^\circ$. Based on this method, a superhydrophobic hole on Al rod was also fabricated to develop a new transfer-pipette equipped with an optimised pressure-generation device, for the purpose of losslessly manipulating water droplets with a large-range volume. Since the applied driving force is far less than the threshold pressure, the lossless manipulation of water droplets can be logically operated. The results show that the operable minimum volume and maximum volume of the certain water droplet are both determined by the diameter of hole. Therefore, in order to manipulate a water droplet with a certain volume, we just need to choose a suitable diameter of hole. The operable limiting volume of the droplet reaches to $140.4 \mu\text{L}$ showing a large-range operable volume. This droplet manipulating method, which shows the reversible and repeatable property, has potential prospects in the field of the liquid transportation, transfer of precious reagents and droplet micro-reactors.

5. Acknowledgments: This work was financially supported by National Natural Science Foundation of China (NSFC, grant no. 51605078), and the Fundamental Research Funds for the Central Universities (grant no. DUT17JC25).

6 References

- [1] Duncombe T.A., Erdem E.Y., Shastry A., *ET AL.*: 'Controlling liquid drops with texture ratchets', *Adv. Mater.*, 2012, **24**, (12), pp. 1545–1550
- [2] Yang X., Song J., Zheng H., *ET AL.*: 'Anisotropic sliding on dual-rail hydrophilic tracks', *Lab Chip*, 2017, **17**, (6), pp. 1041–1050
- [3] Mertaniemi H., Jokinen V., Sainiemi L., *ET AL.*: 'Superhydrophobic tracks for low-friction, guided transport of water droplets', *Adv. Mater.*, 2011, **23**, (26), pp. 2911–2914
- [4] Watanabe M.: 'Surface-directed channels filled with organic solvents', *Lab Chip*, 2009, **9**, (8), p. 1143
- [5] Hu H., Yu S., Song D.: 'No-loss transportation of water droplets by patterning a desired hydrophobic path on a superhydrophobic surface', *Langmuir*, 2016, **32**, (29), pp. 7339–7345
- [6] Sun T., Qing G.: 'Biomimetic smart interface materials for biological applications', *Adv. Mater.*, 2011, **23**, (12), pp. H57–H77
- [7] Lehmann U., Vandevyver C., Parashar V.K., *ET AL.*: 'Droplet-based DNA purification in a magnetic lab-on-a-chip', *Angew. Chem. Int. Ed.*, 2006, **45**, (19), pp. 3062–3067
- [8] Zhao Y., Fang J., Wang H., *ET AL.*: 'Magnetic liquid marbles: manipulation of liquid droplets using highly hydrophobic Fe_3O_4 nanoparticles', *Adv. Mater.*, 2010, **22**, (6), pp. 707–710
- [9] Tang X., Zhu P., Tian Y., *ET AL.*: 'Mechano-regulated surface for manipulating liquid droplets', *Nat. Commun.*, 2017, **8**, p. 14831
- [10] Taniguchi T., Torii T., Higuchi T.: 'Chemical reactions in microdroplets by electrostatic manipulation of droplets in liquid media', *Lab Chip*, 2002, **2**, (1), pp. 19–23
- [11] Lu Y., Sathasivam S., Song J., *ET AL.*: 'Robust self-cleaning surfaces that function when exposed to either air or oil', *Science*, 2015, **347**, (6226), pp. 1132–1135
- [12] Liu K., Du J., Wu J., *ET AL.*: 'Superhydrophobic gecko feet with high adhesive forces towards water and their bio-inspired materials', *Nanoscale*, 2012, **4**, (3), pp. 768–772
- [13] Li J., Jing Z., Zha F., *ET AL.*: 'Facile spray-coating process for the fabrication of tunable adhesive superhydrophobic surfaces with heterogeneous chemical compositions used for selective transportation of microdroplets with different volumes', *ACS Appl. Mater. Interfaces*, 2014, **6**, (11), pp. 8868–8877
- [14] Li J., Liu X., Ye Y., *ET AL.*: 'Gecko-inspired synthesis of superhydrophobic ZnO surfaces with high water adhesion', *Colloids Surf. A*, 2011, **384**, (1–3), pp. 109–114
- [15] Gong G., Wu J., Liu J., *ET AL.*: 'Bio-inspired adhesive superhydrophobic polyimide mat with high thermal stability', *J. Mater. Chem.*, 2012, **22**, (17), pp. 8257–8262
- [16] Huang J., Lai Y., Wang L., *ET AL.*: 'Controllable wettability and adhesion on bioinspired multifunctional TiO_2 nanostructure surfaces for liquid manipulation', *J. Mater. Chem. A*, 2014, **2**, (43), pp. 18531–18538
- [17] Sun T., Qing G.: 'Biomimetic smart interface materials for biological applications', *Adv. Mater.*, 2011, **23**, (12), pp. H57–H77
- [18] Jin M., Feng X., Feng L., *ET AL.*: 'Superhydrophobic aligned polystyrene nanotube films with high adhesive force', *Adv. Mater.*, 2005, **17**, (16), pp. 1977–1981
- [19] Cho W.K., Choi I.S.: 'Fabrication of hairy polymeric films inspired by geckos: wetting and high adhesion properties', *Adv. Funct. Mater.*, 2008, **18**, (7), pp. 1089–1096
- [20] Yuan C., Huang M., Yu X., *ET AL.*: 'A simple approach to fabricate the rose petal-like hierarchical surfaces for droplet transportation', *Appl. Surf. Sci.*, 2016, **385**, pp. 562–568
- [21] Yu X., Zhong Q., Yang H., *ET AL.*: 'Mussel-inspired modification of honeycomb structured films for superhydrophobic surfaces with tunable water adhesion', *J. Phys. Chem. C*, 2015, **119**, (7), pp. 3667–3673
- [22] Liang W., Zhu L., Li W., *ET AL.*: 'Facile fabrication of binary nano-scale interface for no-loss microdroplet transportation', *Langmuir*, 2016, **32**, (22), pp. 5519–5525
- [23] Li J., Ling J., Yan L., *ET AL.*: 'UV/mask irradiation and heat induced switching on-off water transportation on superhydrophobic carbon nanotube surfaces', *Surf. Coat. Technol.*, 2014, **258**, pp. 142–145
- [24] Ding C., Zhu Y., Liu M., *ET AL.*: 'PANI nanowire film with underwater superoleophobicity and potential-modulated tunable adhesion for no loss oil droplet transport', *Soft Mat.*, 2012, **8**, (35), pp. 9064–9068
- [25] Cheng Z., Lai H., Du M., *ET AL.*: 'Super-hydrophobic surface with switchable adhesion responsive to both temperature and pH', *Soft Mat.*, 2012, **8**, (37), p. 9635
- [26] Hong X., Gao X., Jiang L.: 'Application of superhydrophobic surface with high adhesive force in no lost transport of superparamagnetic microdroplet', *J. Am. Chem. Soc.*, 2007, **129**, (6), pp. 1478–1479
- [27] Seo J., Lee S., Han H., *ET AL.*: 'Gas-driven ultrafast reversible switching of super-hydrophobic adhesion on palladium-coated silicon nanowires', *Adv. Mater.*, 2013, **25**, (30), pp. 4139–4144
- [28] Yong J., Yang Q., Chen F., *ET AL.*: 'Reversible underwater lossless oil droplet transportation', *Adv. Mater. Interfaces*, 2015, **2**, (2), p. 1400388
- [29] Wu D., Wu S., Chen Q., *ET AL.*: 'Curvature-driven reversible in situ switching between pinned and roll-down superhydrophobic states for water droplet transportation', *Adv. Mater.*, 2011, **23**, (4), pp. 545–549

- [30] Song J., Huang L., Lu Y., *ET AL.*: 'Fabrication of long-term underwater superoleophobic Al surfaces and application on underwater lossless manipulation of non-polar organic liquids', *Sci. Rep.*, 2016, **6**, (1), p. 31818
- [31] Song J., Huang S., Hu K., *ET AL.*: 'Fabrication of superoleophobic surfaces on Al substrates', *J. Mater. Chem. A*, 2013, **1**, (46), p. 14783
- [32] Liu J., Chen F., Zheng H., *ET AL.*: 'Adjusting the stability of plasma treated superhydrophobic surfaces by different modifications or microstructures', *RSC Adv.*, 2016, **6**, (83), p. 79437
- [33] Zang D., Zhu R., Zhang W., *ET AL.*: 'Stearic acid modified aluminum surfaces with controlled wetting properties and corrosion resistance', *Corros. Sci.*, 2014, **83**, p. 86
- [34] Wang Q., Zhang B., Qu M., *ET AL.*: 'Fabrication of superhydrophobic surfaces on engineering material surfaces with stearic acid', *Appl. Surf. Sci.*, 2008, **254**, (7), p. 2009
- [35] Feng L., Zhang H., Mao P., *ET AL.*: 'Superhydrophobic alumina surface based on stearic acid modification', *Appl. Surf. Sci.*, 2011, **257**, (9), pp. 3959–3963
- [36] Lakshmi R.V., Basu B.J.: 'Fabrication of superhydrophobic sol–gel composite films using hydrophobically modified colloidal zinc hydroxide', *J. Colloid Interf. Sci.*, 2009, **339**, (2), pp. 454–460
- [37] Saleema N., Farzaneh M.: 'Thermal effect on superhydrophobic performance of stearic acid modified ZnO nanotowers', *Appl. Surf. Sci.*, 2008, **254**, (9), pp. 2690–2695
- [38] Mates J.E., Schutzius T.M., Qin J., *ET AL.*: 'The fluid diode: tunable unidirectional flow through porous substrates', *ACS Appl. Mater. Interfaces*, 2014, **6**, (15), pp. 12837–12843
- [39] Widom B.: 'Capillarity and wetting phenomena: drops, bubbles, pearls, waves', *Phys. Today*, 2004, **57**, (12), pp. 66–67