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On-chip microfluidic generation of monodisperse bubbles for liquid interfacial tension measurement

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ABSTRACT

A novel microfluidic method for measuring liquid interfacial tension using monodisperse microbubbles generated *in situ* has been proposed. Instead of bulky gas supply used in traditional microfluidic devices, microbubbles are efficiently generated *via* water electrolysis in the devices. Since the bubble formation frequency is related to the interfacial tension of liquids used, thus, precisely measuring the interfacial tension of liquids in microfluidics can be achieved. In addition, it is found that during the microbubble formation, the electrochemical potential fluctuates regularly at controlled electrolysis current, and the fluctuating period depends on the microbubble generation rate. Therefore, the change in electrochemical potential can be directly used to monitor the bubble formation process, which avoids the use of an external optical detection system. As demonstration, the interfacial tension of isopentanol solutions with different concentrations was measured, and the results show good agreement with the ones obtained using the maximum bubble pressure method, confirming the accuracy of the present method. The proposed strategy offers a simple, low cost and accurate solution to measure the liquid interfacial tension confined in microfluidic channels. The present platform is easily constructed and facilely manipulated in common laboratories, which is expected to be widely used in microfluidic-based research and application fields.

1. Introduction

In the past two decades, the miniaturized and high throughput techniques using microfluidic devices have brought new opportunities for development of energy conversion [1], bioanalysis [2,3], chemical reaction [4], mass separation [5], pharmaceutical delivery [6], and clinical diagnostics [7]. Compared to the bulk systems, the microfluidic devices require less amount of reagents, and allow for much faster analysis speed and higher degree of integration. Particularly, with the channel size downscaling to microscale, the liquid property and dynamics in the channel will be mainly dominated by the viscous shear force and interfacial force, whereas the buoyancy force and inertial force become negligible [8]. Thus, the interfacial tension plays a crucial role in micro-electromechanical devices and lab-on-chips, typically overwhelming gravity and inertia effects that are significant in bulk systems [9]. The unique properties of the microfluidic interfacial tension offer significant advantages in the fields of liquid displacement [10], mixing [11], interface shaping [12], energy conversion [13], and mechanical transduction [14]. However, the precise characterization of interfacial tension in microfluidics yet remains challenging, since most methods for measuring interfacial tensions of bulk systems relying on gravity and other driving forces cannot not be directly downscaled to microchannels [15].

To date, several strategies have been successfully developed to characterize the interfacial tension in microfluidic systems [16–31]. For example, Hudson and co-workers reported a microfluidic approach for rapidly measurement of interfacial tension of immiscible fluids [16,17]. Their method rested upon droplet deformation dynamics by an extensional gradient flow field, which were imaged using an optical microscopy with a monochromatic CCD camera. The measured data showed good agreement with the existing data. Nguyen et al. developed a T-junction microfluidic sensor for measuring gas-liquid interfacial tension by combing with an optical detection technique [18]. The results showed a clear relationship between the interfacial tension and microbubble formation frequency. Luo's group studied the liquid-liquid interfacial tension on devices with different microstructured [21,22]. These methods allow successful and accurate determination of interfacial tension at microscale. Recently, a noninvasive microfluidic method for interfacial tension measurement was presented [31]. They used the dynamic light scattering technique to monitor the resonance of

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waves propagating at liquids interfacial, which is related to the liquid interfacial intension. Although accuracy and precision need further elucidation, this method is expected to become a powerful tool in analysis of microforces. The above-mentioned approaches have greatly advanced the development of on-chip interfacial tension characterization. However, in all these work, either bulky microscope detection system or additional gas supply and force sensor is required, which significantly increases the overall footprint, cost and complexity of the platform. It is desirable to develop simple, low cost and accurate analytical approaches for measuring liquid interfacial forces in microfluidic systems.

Electrochemical techniques are of low cost, simplicity, and good compatibility with microfluidic devices, they have played important roles in moving forward the development of microfluidic systems in various research and application fields [32,33]. Herein, we propose an on-chip electrochemical method for measuring liquid interfacial tension in microfluidic systems. The monodisperse microbubbles are efficiently and steadily generated *via* electrolysis of water in microchannel using a potentiostat. Results show that there exists a clear relationship between liquid interfacial tension and microbubble formation rate, which allows the measurement of liquid interfacial tension in microfluidics. In addition, it is observed that at a constant electrolysis current, the electrochemical potential oscillates regularly during the microbubbles generation process. The oscillation frequency agrees well with the microbubble formation rate, and thus direct monitoring of the bubble formation process in real-time is possible. As demonstration, different concentrations of isopentanol solutions are used as model system to be investigated. The achieved data are in consistent with the values obtained from the maximum bubble pressure method. The present strategy takes advantage of simple and sensitive electrochemical technique, avoiding the use of additional gas supply and bulky optical detection system, and thus it is promising in detection of interfacial tension and other forces in microfluidic systems.

2. Experiment

2.1. Chemicals and materials

Phosphate buffer (PBS, pH 7.4) solution was used as the buffer. Isopentanol was from Nanjing Chemical Reagent Company. Polydimethylsiloxane (PDMS) precursor and curing agent (Sylgard 184) were from Dow Corning, Midland, MI. All the chemicals and solvents were of analytical purity and were used as received. All aqueous solutions were prepared from deionized water (18 MΩ cm, PURELAB Classic, PALL, USA), and were kept in a freezer to prevent deterioration. All liquid samples were filtered with a 0.22 μm syringe filter to remove particulates before use.

2.2. Fabrication of microfluidic chip

Standard soft-lithographic technique was used for microfluidic chip fabrication. The fabrication process was schematically shown in Fig. 1. The microfluidic device composed of a PDMS substrate embedded with a Pt electrode and a PDMS cover with microchannels. For fabrication of the PDMS cover sheet, PDMS was directly casted over an SU-8 photoresist mold on a silicon substrate fabricated by photolithography as previously described [34]. Typically, PDMS precursor and curing agent (Sylgard 184, Dow Corning, Midland, MI) with a 10:1 wt ratio were mixed thoroughly, and then placed in a vacuum box under a reduced pressure to remove air bubbles. After that, the mixture was poured over the master and cured at 60 °C. The cured PDMS film with microchannel was then peeled off the master and cut into proper size. For fabrication of the PDMS substrate, a Pt wire was first placed on the glass sheet. Then, PDMS was cured on the glass surface as described above. When the cured PDMS film was peeled off from the glass, the Pt electrode was embedded in PDMS substrate. Finally, the PDMS slab with designed microchannel was brought in contact with the PDMS substrate implanted with Pt electrode to form a complete microfluidic device. In the present work, the width and depth of microchannel were respectively 75 μm, the length of the microchannel is 2 cm.

2.3. Instrumentation and setup

An Electrochemical Workstation (CHI 1140, Shanghai Chenhua Instrument Company, China) was used for generating monodisperse microbubble, and simultaneously monitoring the microbubble formation process in real-time. An inverted fluorescence microscope (Leica, Dmire2, Germany) equipped with a highly sensitive CCD video camera (S45, Canon, Japan) was used for optical tracking microbubble formation and releasing process. NIS-elements BR 2.30 software (Nikon) was used for camera control and image processing.

2.4. Electrochemical generation of microbubbles and interfacial tension measurement

The monodisperse microbubbles were electrochemically generated on the microchip as illustrated in Fig. 1. The pre-embedded platinum (Pt) electrode in microfluidic chip was used as the cathode. An external Pt electrode placed in the reservoir was used as the anode. For liquid interfacial tension measurement, PBS buffer with different concentrations of isopentanol was first filled in microchannel. Then, chronopotentiometry (at a constant current) was used for water electrolysis and microbubble formation. The interfacial tension measurement was performed based on microbubble formation rate.

2.5. Determination of interfacial tension of isopentanol solution in bath system

Different concentrations of isopentanol solutions were prepared in volumetric flask. The maximum bubble pressure method was used for interfacial tension determination of isopentanol solutions in bath system as described prevsiouly [35]. The setup was illustrated in Fig. S1 in the supporting information.

3. Results and discussion

3.1. Formation of monodisperse bubbles on microfluidic chip

The monodisperse microbubble was electrochemically generated on chip using galvanostat method (at a constant current). As illustrated in Fig. 2A, when a constant current is applied between anode and cathode, electrolysis of water occurs. Hydrogen microbubbles will be formed at the cathode and oxygen at the anode following the electrochemical Eqs. (1) and (2).

$$Anode: H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2 \quad (1)$$

$$Cathode: 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (2)$$

The generated gas firstly nucleates on the electrode surface, then gradually grows up. At the moment when the drag force of the electrode equals to the interfacial tension of the microbubble, the microbubble releases from the electrode surface to the microchannel (Fig. 2B). To confirm the generation of microbubbles, an inverted fluorescence microscope was use to track the microbubbles formation process in real-time. It is known from Eqs. (1) and (2), two folds of gas volume (H_2) will be generated at the cathode as compared to the one (O_2) at the anode. For ease of observation, hydrogen microbubbles were monitored in the following experiments. As shown in Fig. 2C, the monodisperse microbubbles could be successfully produced using the present method. In comparison, constant potential approach was also used for microbubble generation. In this case, the formed microbubbles are not