Separation and Electrochemical Detection Platform for Portable Individual PM2.5 Monitoring

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***Abstract*--Airborne particulate matter (PM) pollution, especially fine particles with a diameter of 2.5 µm or smaller (PM2.5), has caused severe air quality issues that threaten human life and contribute to global mortality. Thus a low cost, portable or wearable platform for individual PM2.5 monitoring is of great interest. This paper introduces a platform for portable real-time PM2.5 monitoring that combines a particle separation microfluidic channel and electrochemical detection. The microfluidic device utilizes an I-shape pillar based deterministic lateral displacement method to achieve high separation efficiency of different particle sizes. Electrochemical detection was implemented for particles measurement to achieve high sensitivity and simplify the instrumentation compared to conventional optical methods. Both separation and detection results show that this platform is a promising option for portable PM2.5 monitoring.**

Keywords – I-shape pillar, DLD separation, electrochemical detection, CMOS, PM2.5

I. INTRODUCTION

Particulate matter (PM), also known as particle pollution, as defined by the US Environmental Protection Agency (EPA), is a complex mixture of small particles and liquid droplets consisting of a number of components including acids (such as nitrates and sulfates), organic chemicals, metals, soil or dust particles, and allergens (such as fragments of pollen and mold spores) [1] Both long- and short-term PM exposures, especially to fine particles (PM2.5, particles of diameter 2.5 µm or less) represent severe threats to human health, causing high cancer incidence and mortality, and are especially harmful to elders and infants [2]. Although human exposure to PM2.5 varies significantly with an individual's lifestyle and locations visited throughout the day, existing commercial monitoring systems are bulky and expensive and thus are not suitable for individual exposure monitoring. As technologies for miniaturized sensors advance there is a growing interest in low-cost and portable or even wearable systems that can provide real-time PM2.5 monitoring [3].

A miniaturized PM2.5 monitoring system would generally consist of a classification stage and a concentration detection module. Microfluidics technology, which has been successfully applied in cell sorting and particle counting [4], provides a convenient way to implement particle classification for PM2.5 exposure monitoring. Inertial impactors for ambient air sampling, have been reported [5], but they suffer from particle build up and oil requirement issues. A microfluidic technology based on the centrifugal force differences in a curved microchannel to continuously size airborne particles for aerosol monitoring was reported to achieve 80% separation efficiency [6]. Recently, an I-shaped based deterministic lateral displacement (DLD) device was reported to achieve 100% separation efficiency for non-spherical particles [7], [8].

For PM2.5 detection, mass detection and optical methods are popularly used. PM detection based on the gravimetric analysis with quartz crystal microbalance (QCM) has been reported [9]. QCM can correlate resonant frequency shifts to particle mass; however, the overloaded issue and particle flake off effect due to fast oscillation are obstacles for QCM detection. Optical methods for PM detection based on light-scattering have also been reported by several groups [10, 11]. However, optical systems are complicated, expensive and bulk and thus not well suitable for low-cost portable application. In contrast, electrochemical detection can offer precise PM2.5 inspection, for example using AC impedance detection to measure impedance change when particles deposit on an electrode. Furthermore, the instrumentation for electrochemical sensors can be readily formed in CMOS chips [12], and highly integrated electrochemical sensor system to be realized in a miniaturized format [13].

This paper introduces the first PM2.5 monitoring platform that combines the DLD microfluidic separation and electrochemical detection toward a solution for low-cost, real-time, portable personal PM2.5 exposure monitoring. This platform was demonstrated to efficiently separate and detect particles based on their size.

II. INTEGTATED PARTICLE SEPARATION PLATFORM

As shown in Fig 1, the new PM2.5 monitoring platform consists of a microfluidic separation part and an electrochemical detection part. The separation part adopts the deterministic lateral displacement (DLD) method [8] that utilizes asymmetric bifurcation of laminar flow around pillar arrays for particle separation. Particles choose the path deterministically on the basis of individual size, and all particles follow equivalent migration paths based on the given size, which produces high separation efficiency with very high size resolution. By carefully designing the pillar

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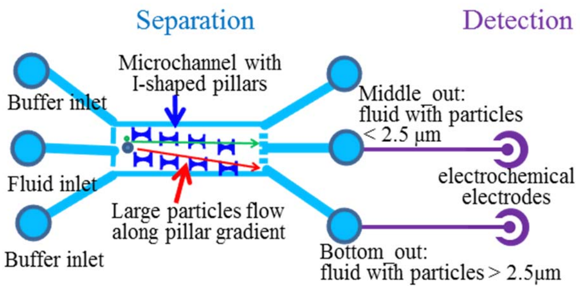

Fig 1. Platform for PM2.5 monitoring consisting of separation and detection components.

size, spacing and array gradient, a DLD microchannel device can separate particle above a critical size. Particles larger than the critical size are bumped off their initial flow path and displaced laterally to follow the designed pillar gradient. In contrast, small particles less than the critical size will continually flow along their original fluid streams unaffected by the pillar array.

Based on the DLD method, I-shaped pillars have been reported that will induce the rotation of the non-spherical particle that can enhance the separation efficiency [7]. Because PM is also irregularly shaped, we chose to incorporate the I-shaped pillar concept into our separation microchannel to increase separation efficiency.

Electrochemical measurement methods typically have high sensitivity, repeatability and selectivity and are good candidates for battery-power portable/wearable systems due to their low power consumption. For example, our group has reported a robust flexible electrochemical gas sensing system designed for portable sensing application [14]. For PM2.5 detection, square-wave anodic stripping voltammetric method has been reported for electrochemical quantification of metal ions in PM sample [15]. To verify PM detection in our system utilizing electrochemical method, an AC electrochemical impedance method was chosen to electrically inspect particles after separation. Nonconductive particles depositing on the surface of a working electrode (WE) will increase the impedance within the double layer on the electrode surface, which can be detected by electrochemical instrumentation. Compact, low-power electrochemical circuits and CMOS instrumentation chips have been widely studied, making electrochemical methods a good choice for portable/wearable systems.

III. FABRICATION OF DLD SEPARATION

A. *I-shaped DLD separation design*

COMSOL Multiphysics fluid flow simulation was performed for the I-shaped pillar array to study the fluidic velocity profile and to understand how the pillar array will affect the laminar flow in both liquid an air samples. As shown in Fig 2, the groove area between pillars introduces a disturbance in peak velocity streamline path. This groove will introduce rotation of non-spherical particles to enhance the separation efficiency.

The critical separation diameter can be calculated by [7]:

$$D_C = 1.4gN^{-0.48}$$

where D_C is the critical separation diameter, g is is the gap size between pillars and N is number of rows per shift in columns. Based on calculations and simulation results, to achieve a 2.5 µm critical separation size, the height of the overall microchannel was set as 15 µm and the I-shaped pillars were chosen to be 15 µm × 15 µm with the space between pillars set to 10 µm. The overall microchannel width (W) was set to 2mm and the length (L) to 20mm and the tiled gradient of the pillar array was set to 2.87º, as shown in Fig. 3. The results were very similar for both liquid and air samples.

B. *I-shaped DLD microchannel fabrication*

The separation device was designed to consist of a pillar-

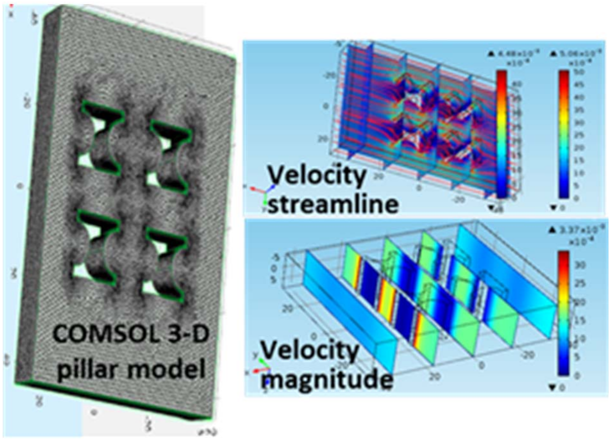

Fig 2. COMSOL 3-D model (left) and simulation results (right) for I-shaped pillar in a DLD microchannel.

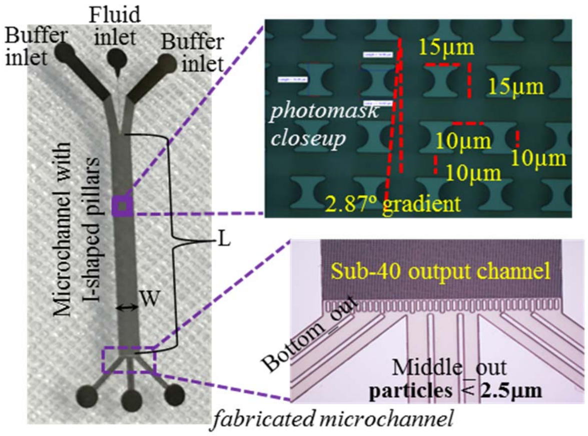

Fig. 3. Fabricated microchannel with I-shaped DLD pillars and close up views showing pillar dimensions (top right) and routing of the 40 output microchannels to three fluid outlets where particles are separeated by size.

containing microchannel formed in a silicon wafer using deep reactive ion etching (deep-RIE) and a molded PDMS lid to cap the microchannel. To ensure the sample entered in the middle of the microchannel, the sample inlet was placed in the middle of the channel while buffer inlets enter to the left and right of the sample inlet, as shown in Fig. 3. Inside the microchannel, I-shaped pillar array was etched to form a long separation channel with 40 columns at the output end that are then binned into three fluid outlets. Based on design parameters, the "Bottom_out" outlet, shown on the left in Fig. 3, should contain all particles larger than 2.5 µm while the smaller particles of main interest for PM2.5 separation should appear in the "Middle_out" outlet.

To perform deep-RIE of the microchannel and pillar array in a silicon wafer, the wafer was first covered by a patterned photoresist mask. HDMS was first applied to improve adhesion and then SPR220 photoresist was spin-coated at 2000 rpm to form a 3.15 µm photoresist layer. A 90 s prebake at 115ºC and 5 s exposure through the photomask were then performed and followed by a 90 s post-bake at 115ºC. AZ 726 was then used to develop the SPR220 to transfer the pattern. The device was then etched with STS Pegasus using deep-RIE to produce approximately 15 µm depths.

For the PDMS lid, a soft lithography fabrication process was used. Then, the inlets and outlets were punched into the otherwise solid PDMS block. The PDMS lid and the silicon microchannel were then bonded after oxygen plasma treatment of both surfaces. During the bonding process, a mask aligner was used to align the inlets and outlets on the two components. Finally, the bonded device was thermally treated in an oven at 130ºC.

IV. RESULTS AND DISCUSSION

A. Particle separation results

To verify particle separation, two different solutions with polystyrene beads were prepared, one containing 1 µm particles and the other containing 10 µm particles. Before introducing the sample solution, 1% w/v Pluronic F127 (Sigma Aldrich, USA) and DI-water were pumped into the microchannel to avoid particle clustering and particle adhesion to channel walls. Using the test setup shown in Fig. 4(a), a sample solution containing a diluted mix of 1 µm and 10 µm particles was pumped into the sample inlet at 0.5 µL/min while a phosphate-buffered saline (PBS) buffer solution was pumped into both buffer inlets at 0.2 µL/min using three syringe pumps. Fluids exiting the three outlets were collected in separate reservoirs, as shown in Fig. 4(a).

During the separation process, particle movement inside the channel was recorded on videos that clearly show the 10 µm large particles being bumped by the pillars to flow along the pillar gradient toward the Bottom_out outlet. As desired, the 1 µm small particles flowed along their initial flow paths to concentrate at the Middle_out outlet (since particle sample was injected in the middle of the microchannel). Once the separation process was completed, droplets from each of the collection reservoirs were extracted by pipette and inspected under a microscope. The results in Fig. 4(b) show that the Bottom-out outlet contained all of the 10 µm particles (none observed in other outlets) while the 1 µm particles were largely contained in the Middle-out outlet.

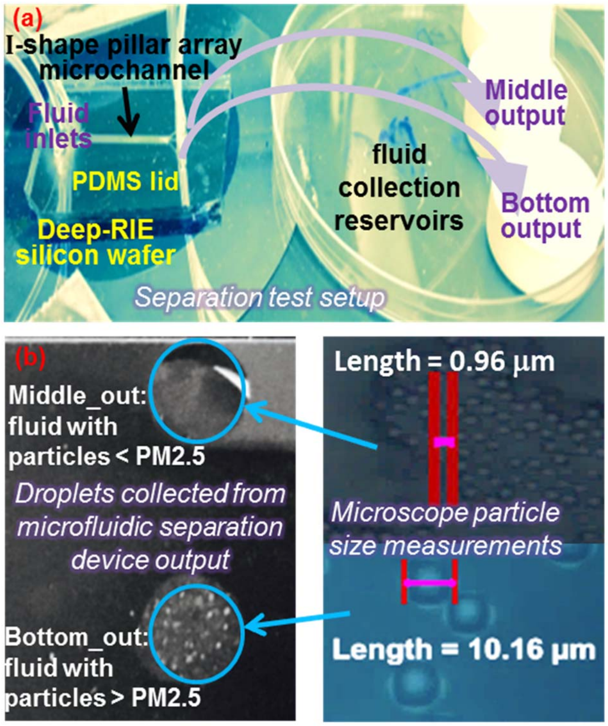

Fig. 4. Particle separation device test setup and results: (a) the DLD separation device consits of a deep-RIE silicon microchannel and PDMS lid and separates large partilce to the bottom (Bot) output; (b) Droplets collected from the output and measured by a microscope show that the particles were properly separated.

B. AC impedance detection results

To demonstrate electrochemical detection of particle-containing solutions, commercial carbon electrodes, shown in Fig. 5(a) were used to perform AC impedance measurements. Commercial polystyrene bead solutions (Sigma-Aldrich) were obtained with 1µm particles and 10µm particle. Each particle-containing solution was diluted by a factor of 10 and treated under ultrasonic for over 1 hour before testing to ensure the beads were not clustered. Then, 4 mL of each particle-containing solution was added to a separate electrolyte solution containing of 8 mL KCl, 16 mL $K_3[Fe(CN)_6]$, 52 mL DI water. A third sample was prepared in a similar manner but contained no polystyrene beads.

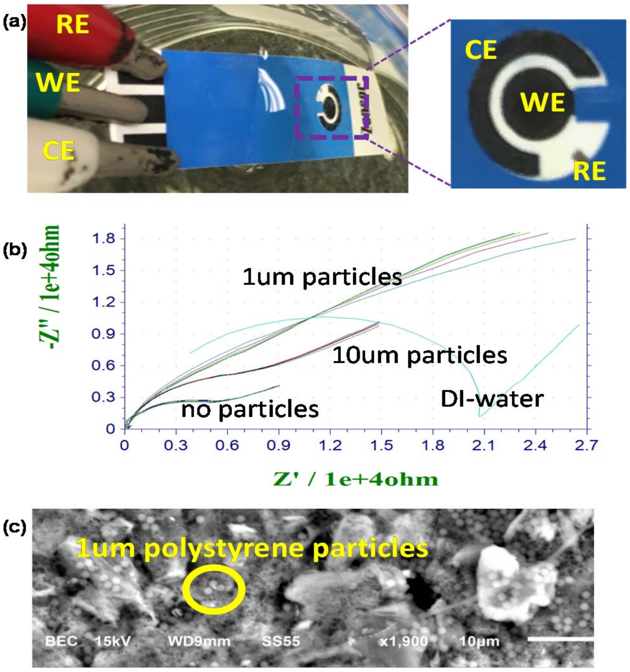

Fig. 5. (a) Commercial carbon electrodes used for AC impedance measurements; (b) Nyquist plots collected from the AC impedance for three samples with different particle sizes producing clearly distinguishable results; (c) SEM inspection show that the 1-μm particles were deposited on electrodes

A carbon electrode was then inserted into each of the three samples, and AC electrochemical impedance measurements were performed. The voltage amplitude was set to 0.5 V and the frequency was swept from 1 Hz to 1 MHz using a CHI 760 (CH Instrument, USA) electrochemical instrument. The resulting Nyquist plots in Fig 5(b), shows that electrolyte without particle, with 1 μm particle solution and with 10 μm particle solution have distinctly different impedance response, verifying that electrochemical impedance can effectively detect samples with different particle sizes. For each sample, five repetitive tests were performed, and the results show very good repeatability. These preliminary results demonstrate the feasibility of this platform for PM separation and measurement and lay the groundwork for future testing with real PM2.5 samples collected from urban environments.

After AC impedance detection, the electrode surface was also checked using scanning electron microscope (SEM). As shown in Fig 5(c), 1 μm particles were found on the surface of carbon electrode after electrochemical detection, which further supports the observed AC impedance change due to the particle deposition.

V. CONCLUSION

This paper introduced a platform for portable, real-time PM2.5 monitoring that combines a microfluidic I-shaped DLD particle separation device and electrochemical detection methods. The fabricated I-shaped DLD separation device was observed to provide nearly 100% separation efficiency for the designed critical separation size. AC electrochemical impedance measurements were shown to identify particle size with high sensitivity. The demonstrated platform is well suited for implementation into low-cost wearable individual real-time monitoring applications.

VI. ACKNOWLEDGMENT

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