Experimental Section

Device fabrication. The PDMS microfluidic devices were manufactured through replica molding of masters using multilayer soft lithography prototyping technique. Master molds were fabricated by standard photolithography technique.[1] The devices consisted of two layers, flow layer and control layer. The scheme is shown in Figure S1. The master of flow layer was fabricated using a multi-step photolithography process consisting of two different resist height profiles: rounded profile (~19 μm high) for flow channels that needed be completely sealed by microvalve, and squared profile (60 μm high) for fluid flow and droplets transport. Briefly, the rounded layer was first made with PZ positive photoresist, after which SU8-2025 negative photoresist was spin on the positive-layer master. The control master is a single-layer mold with squared profile of 35 μm height made with SU8-2025 photoresist. The control layer was at the bottom of flow channel. Access ports were created by punching the PDMS with 3mm-diameter needle. After treatment with oxygen plasma, the PDMS slabs with flow layer and control layer were bonded to glass slides. Then the sealed devices were placed in a 100° C oven overnight to recover the hydrophobicity of PDMS.

Negative pressue supply. Negative pressure was supplied by connecting the end reservoir of the device to a 100 ml bottle which has been evacuated by a syringe. The degree of negative pressure could be controlled by varying the volume of air evacuated, which could be calculated in the form of kPa according to

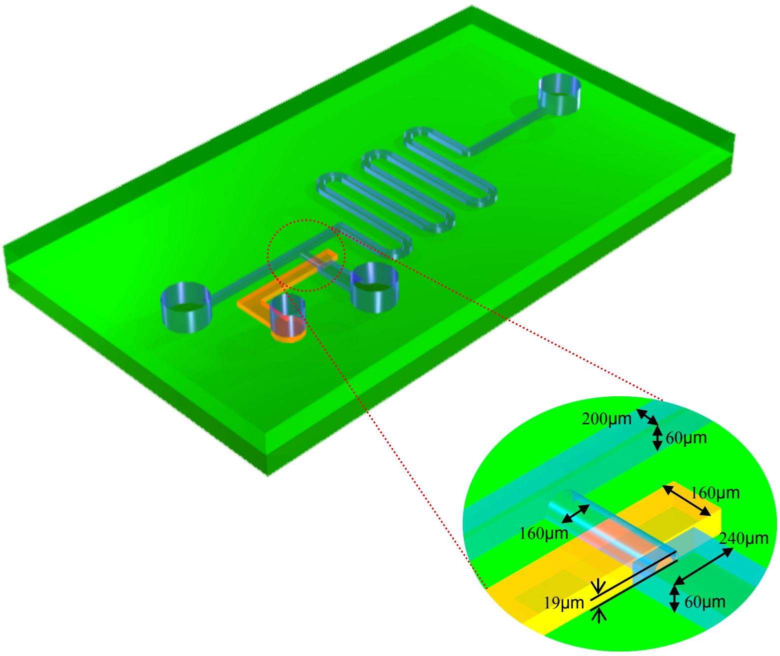
$$\Delta P = P_0 V/(100+V)$$

Where ΔP was the degree of negative pressure; P_0 was the atmospheric pressure and was assumed to be 100kPa; V was the volume of air evacuated, 100 referred to the volume of bottle, the unit here was milliliter.

Setup. All images and movies of droplets were recorded by an inverse fluorescence microscope (Olympus Ⅸ 71, Japan) with a digital CCD camera (Q Imaging, Micro Publisher 5.0 RTV) using bright field illumination. The size of droplets was analyzed based on area, which was obtained by Image-Pro (Media cybernetics, USA). The operation of on-chip pneumatic microvalve was accomplished by a home-made and computer-controlled device that could individually control 16-port solenoid valves (LHDA 0523111H, Lee Co., Westbrook, CT, USA).

Reagents and materials. Oleic acid was used as carrier fluid for demonstration as it could be washed away by ethanol. Other oil such as mineral oil showed similar results. Span 80 was added in oil phase (2.5%, w/w) to stabilize droplets in microchannels. For the ease of imaging, diluted colored ink solution was used as aqueous phase. In the generation of single-content droplet, orange ink solution was used and for the generation of arrays of droplets with distinct composition, orange, blue, brown and green ink solution was used.

[1] B. T. C. Lau, C. A. Baitz, X. P. Dong, C. L. Hansen, *Journal of the American Chemical Society 2007, 129, 454*.



Figuer S1. Schematic diagram of the microfluidic device integrated with pneumatic microvalve for generation of single-content droplets. The flow layer consists of channels of two different profiles: rounded profile (19μm high and 160μm wide) for operation of microvalve and squared profile for fluid flow (oil phase channel: 200μm wide, 60μm high; aqueous phase channel: 240μm wide, 60μm high); the control channel is of squared profile (35μm high and 160μm wide).