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Introduction

1.1 Microfluidics and Its Superiority in Controllable Fabrication of Functional Materials

Microfluidics, or the so-called lab-on-a-chip, has emerged as a distinct new technology since the beginning of 1990s [1]. The dimensions of the microfluidic channels and components are tens to hundreds of micrometers. The microfluidic devices can be used to flexibly manipulate the flow of microvolume fluids in microchannels, which are considered putting the lab on a chip (Figure 1.1). Due to the trend of miniaturization and integration of modern scientific and technological civilization development, microfluidic technology has been widely concerned and valued by the international scientific and industrial communities. In 2006, *Nature* magazine published a special issue on the topic of "*Insight: lab on a chip*," including seven related review papers [1, 2], where the editorial says that it might have the potential to become "a technology for this century." In 2010, *Chemical Society Reviews* published a special issue on the topic of "*From microfluidic applications to nanofluidic phenomena*," including 20 related review papers [3], which shows the promising momentum of development of microfluidic technologies. Since microfluidic technology can accurately manipulate small-volume fluids, it is rapidly extending from the original analytical chemistry platform for microanalysis and microdetection, to high-throughput drug screening, micromixing, microreaction, microseparation, and so on. Due to its excellent ability to control fluid interfaces as well as excellent heat and mass transfer performances, microfluidic technology has become a novel and promising material preparation technology platform (Figure 1.2). Microfluidic technology has emerged in the construction of precisely controllable microstructured new functional materials with high performances, such as microcapsules and microspheres, membranes in microchannels, and superfine fiber materials, and especially shows incomparable creativity and superiority compared with traditional technology in design and preparation of some new functional materials with high added values [4–35].

To sum up, stable phase interface structures of immiscible liquid phase systems that are constructed by the microfluidic technology can be mainly divided into two systems [4]: one is the emulsion droplet system with closed liquid–liquid interfaces, and the second is the laminar flow system with closed
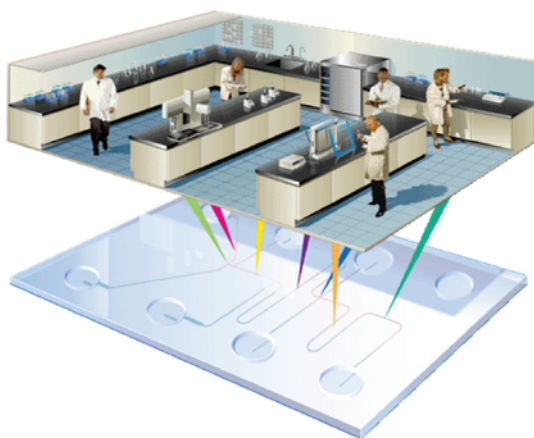
Figure 1.1 Microfluidics: putting the lab on a chip.

Appl Phys Lett, 2003, 83: 4664

Soft Matter, 2010, 6: 3489

Chem Soc Rev, 2009, 38: 2161

Micro mixing

Micro reaction

Micro separation

Micro Analysis

Material fabrication

Excellent control over the interfaces of microfluids, as well as the heat and mass transfer

Science, 2005, 310: 1793
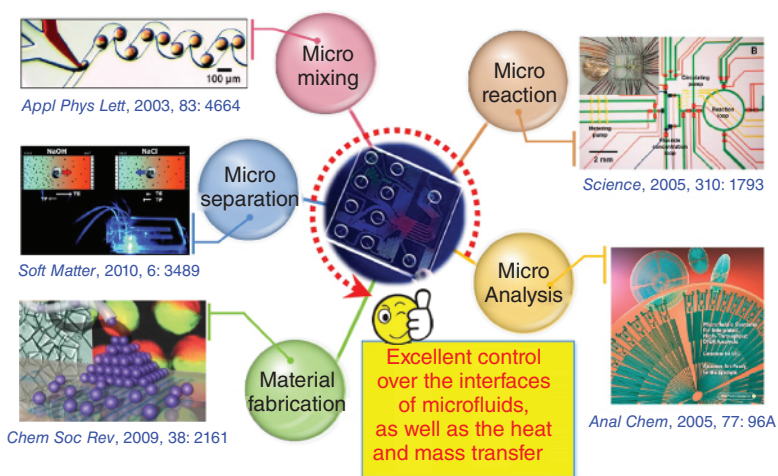
Anal Chem, 2005, 77: 96A

Figure 1.2 Microfluidic technology is becoming a novel technology platform for materials preparation because of its excellent control over the microfluid interfaces as well as the heat and mass transfer.

liquid–liquid interfaces (Figure 1.3). These two microfluidic-constructed stable phase interface structure systems can be used to prepare three categories of high-performance functional materials with accurate and controllable microstructures as follows [4–35]: (i) controllable fabrication of novel microspheres and microcapsules with precise microstructures by using emulsion droplet systems with closed phase interfaces as templates [4, 5, 7–32]; (ii) controllable fabrication of membranes in microchannels by using laminar flow systems with nonclosed layered phase interfaces [6, 33, 36, 37]; and (iii) controllable fabrication of novel microfiber materials by using laminar flow systems with nonclosed annular phase interfaces [4, 10, 34, 38]. As illustrated in Figure 1.3, microfluidic technology shows superior controllability and great potential in the construction of these three kinds of functional materials, and
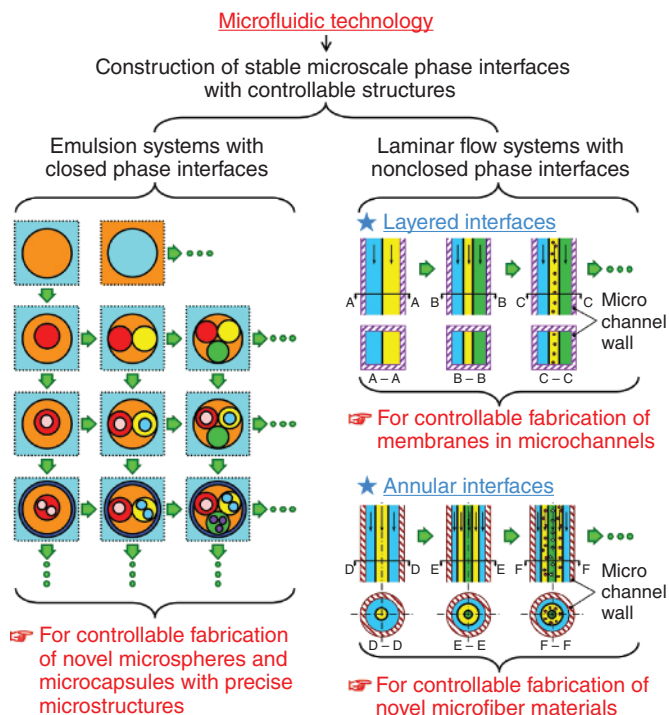
Figure 1.3 The system diagram of microfluidic method for the construction of stable microscale phase interfaces and for controllable preparation of novel functional materials.

can play its unique advantages in controllable construction of new functional materials with new structures, new functions, and high-performance features.

1.2 Microfluidic Fabrication of Microspheres and Microcapsules from Microscale Closed Liquid–Liquid Interfaces

Due to the small size and controllable internal structure, microspheres and microcapsules can be used as microcarriers, microreactors, microseparators, and microstructural units in drug delivery, substance encapsulation, chemical catalysis, biochemical separation, artificial cells, and enzyme immobilization, and have very broad application prospects. Microspheres and microcapsules are generally fabricated by using emulsion droplets with stable closed liquid–liquid interfaces (e.g., single water-in-oil (W/O) or oil-in-water (O/W) emulsions, W/O/W or O/W/O double emulsions, or even more complicated multiple emulsions) as templates, through subsequent polymerization, cross-linking, solvent evaporation, curing, and assembling in emulsion droplets or at interfaces. Traditional methods for the preparation of emulsion droplets are mainly achieved by mechanical stirring or fluid shear; thus, the sizes and the internal

structures of the droplets and the resultant template-fabricated microspheres and microcapsules are difficult to be controlled precisely, which greatly affect the performances and applications of the microspheres and microcapsules.

Microfluidic technology, which can generate emulsion droplets by emulsifying disperse phase to continuous phase through microchannels with co-flow, flow-focusing, or T-junction geometries, can achieve continuous and precise control of the microstructures of emulsion droplets, exhibiting significant superiority in the fabrication of microspheres and microcapsules with controllable size distributions and microstructures.

Researchers from all over the world have made a lot of important progress in the use of microfluidics to construct microscale closed liquid–liquid interfaces and then fabricate monodisperse microspheres and microcapsules [4, 5, 7–32]. In the preparations of microspheres and microcapsules with microfluidic approaches, most of them are focused on the use of microfluidic-generated W/O or O/W single emulsions (as shown in the first row in the upper left corner of Figure 1.3) as templates for preparing monodisperse microspheres, or the use of W/O/W or O/W/O double emulsions (as shown in the second row in the first column of the upper left corner of Figure 1.3) as templates for preparing monodisperse core–shell microcapsules. Some studies have also attempted to prepare some materials with new structures such as multicore microspheres, Janus microspheres, and nonspherical particles by microfluidic technology.

The authors' group controllably constructed multiple emulsion systems with complex microscale multiphase multicomponent liquid–liquid interfaces by building series and parallel microchannels [31]. These emulsions are used as templates for controllably preparing multiphase multicomponent microspheres and microcapsules for the encapsulation of substances [29], as well as new multifunctional microspheres and microcapsules with complex structures [28, 30].

1.3 Microfluidic Fabrication of Membranes in Microchannels from Microscale Nonclosed Layered Laminar Interfaces

Because of the excellent performances in catalysis, separations, purifications, analysis and detection, controlled release, emulsification, and so on, functional membrane materials are considered as one of the important supporting technologies for sustainable development. If the combination of membrane materials and microfluidic technology is obtained, it will play the synergy of the two to achieve the integration of functional materials and components. In this way, it can not only promote the application of membrane materials in microseparation and microanalysis but also provide new catalysis- or reaction-separation coupling technologies for microchemical or microreaction processes, showing very broad application prospects [6]. Therefore, as a new technology platform, membrane-in-microchannel technology is increasingly subject to different disciplines of international attention [6].

In a co-flow microchannel, when immiscible multiphase fluids flows into the same microchannel, stable layered laminar flow patterns can be formed through

microfluidic laminar flow technology [36] ("Layered interfaces" in Figure 1.3). In each phase, the fluid can maintain its flow pattern unchanged; chemical reactions such as polymerization and cross-linking only occur at the liquid–liquid interfaces, forming monolayer or multilayer parallel ultrathin membranes in the microchannels.

The microchannels can be divided into several independent channels by the membranes in microchannels. Due to the selective permeability or adsorption ability of functional membrane materials, selective separation, extraction, detection, and analysis can be realized with the membranes in the microchannels. Catalysts can also be effectively deposited on the membrane surfaces, thereby increasing the specific surface area of the catalytic material within a microchannel, to accelerate the rate of catalytic reaction in the microchannel. In addition, environmental stimuli-responsive smart membranes, which can regulate the effective membrane pore size and permeability in response to the change in physical or chemical signals in the environment, show incomparable superiority over traditional membranes [39]. If the smart membranes can be combined with microfluidics, it will undoubtedly provide efficient technology platform for the intensification of microseparation, microanalysis and detection, microreaction processed, and the enhancement of membrane performances.

Since the fabrication processes of membranes in microchannels are different from traditional membrane preparation processes, so far there are only a few reports on the fabrications of membranes with limited materials such as polyamide and chitosan in microchannels by using microfluidic laminar flow technology [6, 33, 36, 37, 40, 41].

1.4 Microfluidic Fabrication of Microfiber Materials from Microscale Nonclosed Annular Laminar Interfaces

Microfiber materials have a wide range of applications in optoelectronics, biomedicine, chemical industry, light industry, and other fields, wherein the hollow fiber membranes play an important role in the chemical separation processes. Currently, the preparations of microfiber materials are mainly achieved by using melt spinning method, electrospinning method, and other methods, while these methods are still difficult to achieve precise control of the microstructures of microfiber materials or impart multifunctional characteristics. Therefore, it is still necessary to seek new preparation processes and methods for the preparation of microfiber materials, and the microfluidic laminar flow technology is a very promising new method.

With microfluidic laminar flow technology, stable annular laminar flow patterns of immiscible multiphase fluids can be formed in the microchannels [4] ("Annular interfaces" in Figure 1.3). With these stable annular multiphase laminar interface systems as templates, microfiber materials including linear solid microfibers, hollow tubular microfibers, and core–shell composite microfibers can be fabricated by reaction or curing at the liquid–liquid interfaces or inside phases.

Since microfluidic technology enables continuous and accurate control over the annular liquid–liquid interfaces of laminar flows, it can provide optimal design of fibrous material synthesis systems. Therefore, compared with traditional spinning techniques, microfluidic technology has significant advantages in precise regulation and design of microfiber microstructures: it improves performances and imparts multifunctional characteristics of microfiber materials [4, 34, 36, 38, 42–47].

Microfluidic technology has been used to successfully prepare calcium alginate, polyvinyl alcohol, poly(lactic-*co*-glycolic acid), liposomes, chitosan, poly(ether sulfone), and polyacrylonitrile microfibers [34, 38, 42–47], which show excellent flexibility and extraordinary potential in the construction of microscale annular liquid–liquid interfaces and preparation of microfiber materials.

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