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On-Chip Catalytic Microreactors for Modern Catalysis Research

Bin-Bin Xu,[a] Yong-Lai Zhang,*[a] Shu Wei,[a] Hong Ding,[c] and Hong-Bo Sun*[a, b]

Over the past two decades, microfluidics, represented by lab-on-a-chip (LoC) systems, have been developed because of their unique advantages of low reactant consumption, environmental friendliness, high safety, high efficiency, high sensitivity, portability, and easy handling of reactants. The distinguishing features of microfluidics have made the on-chip reactor a highly efficient platform for general chemical experiments, especially catalysis. In this paper, through a brief review of the recent work on microfluidic catalysis, we highlight the importance of on-chip catalytic microreactors. New approaches to the fabrication of on-chip catalytic microreactors and their integration with multifunctional components are briefly introduced. Finally, the current challenges and future perspectives of this up-and-coming field are discussed based on our own opinions. It is believed that, with the progress of interdisciplinary cooperation, microfluidics and catalysis could be complementary sciences; catalysts may play a very important role in LoC systems, and on-chip catalytic microreactors could be a highly efficient experimental platform for modern catalysis research.

Introduction

Recent years have witnessed the rise of micro-total-analysis systems (μTAS), the so-called lab-on-a-chip system (LoC),[1–3] in a broad range of scientific fields that include chemistry,[4] physics,[5,6] biology,[7,8] materials science,[9] pharmaceutics,[10] tissue engineering, and iatrology.[11] To date, despite its short history, innovations in microfluidics have revealed a cornucopia of both new fluidic physics and promising functionalities such as bioanalysis, chemical synthesis, sensitive detection, catalysis, and even immunization therapy.[12–19] Typically, by using microfluidic devices, various laboratory handling units, which include reactant injection, procedure monitoring, and product analysis, could be easily performed inside microchannel networks integrated on a chip with a feature size similar to or even smaller than a credit card.[20–23] As experimental procedures could be performed in a confined space, probably in the scale range from tens to hundreds of microns, only small dosages of reactants (10^{-9}–10^{-18} L) are needed for whole experiments. From a sustainability point of view, the ultralow reactant consumption not only leads to economical experiments but also contributes to negligible waste and high safety. More importantly, the confined reaction space is of benefit to mass/heat transfer, and thus leads to a high reaction rate and high sensitivity. The advantages of microfluidic devices are so distinct that LoC systems are considered to be an efficient and high-throughput experimental platform that is suitable for various scientific fields.[24,25]

Currently, owing to their high efficiency, high sensitivity, safety, and portability, LoC devices are popular for chemical and biochemical assays.[26–30] In the case of microfluid flow, the significantly miniaturized channel size reduces the influence of inertial forces compared to frictional forces that give rise to laminar flow,[31] which enables the spatial control of the liquid composition at subcellular resolution, fast media and temperature changes, and even single-cell handling and analysis.[32,33] Moreover, by taking advantage of the massive parallel processing capability, some microfluidic chips enable high-throughput cell biological experiments.[34] In addition, LoC systems have also been successfully developed to perform a wide range of DNA analyses, which include cell trapping and sorting, cell lysis, DNA extraction and purification, DNA amplification, the polymerase chain reaction (PCR), and DNA detection.[35–42] In the field of biomedical research, microfluidic devices allow more accurate modeling of physiological situations, and thus enable systematic high-volume testing for various aspects of drug discovery.[43] Additionally, microfluidic devices are amenable to be interfaced with various analytical instruments, such as UV/Vis spectroscopy,[44] Raman spectroscopy,[45,46] MS,[28,47] GC, and LC,[48] which further broadens their practical applications.

However, compared with biochemical research, less effort has been devoted to the field of on-chip catalysis, despite the

[a] B.-B. Xu, Dr. Y.-L. Zhang, Dr. S. Wei, Prof. H.-B. Sun
State Key Laboratory on Integrated Optoelectronics
College of Electronic Science and Engineering
Jilin University, 2699 Qianjin Street
Changchun,130012 (People's Republic of China)
Fax: (+86) 431-85168281
E-mail: yonglaizhang@jlu.edu.cn

[b] Prof. H.-B. Sun
College of Physics
Jilin University, 119 Jiefang Road
Changchun, 130023 (People's Republic of China)
E-mail: hbsun@jlu.edu.cn

[c] H. Ding
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry
College of Chemistry
Jilin University, 2699 Qianjin Street
Changchun,130012 (People's Republic of China)

fact that catalysis research based on microfluidic devices possesses a series of distinct advantages. For catalytic reactions inside a microfluidic reactor, the reactants would have a much higher activity because of the spatial confinement. Considering that the generally used microfluidic channel is only tens and hundreds of microns in depth and width, respectively, the significantly increased surface-area-to-volume ratio would lead to intimate contact between diverse reactants and catalysts to give rise to high catalytic activities. In addition, microfluidic devices show improved control over mass and heat transfer superior to that in macroscopic reaction settings, which also contributes to the high reaction rate. In this regard, microfluidic reactors with confined reaction spaces are of considerable importance to modern catalysis research, for instance, in investigations on catalytic mechanisms and in screening optimized catalysts and reaction conditions. Therefore, it is highly desired to bring on-chip catalysis to modern catalysis research.

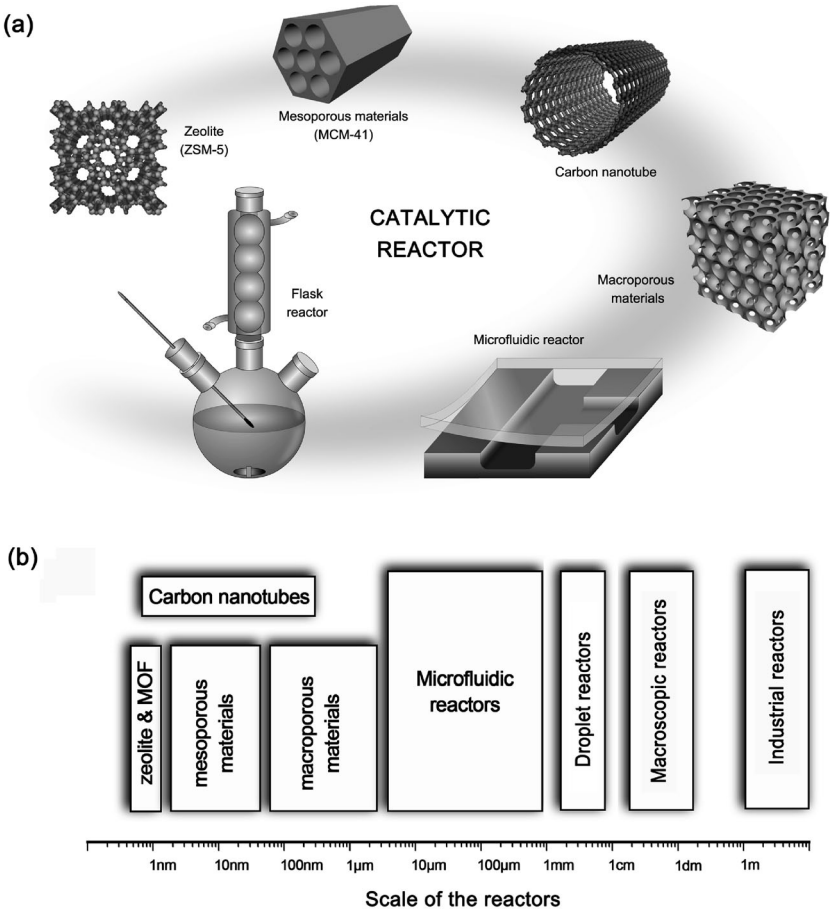

Figure 1. a) An illustration of typical reactors of different sizes. Zeolites, mesoporous materials, carbon nanotubes, macroporous materials, microfluidic devices, and macroscopic instruments have been chosen as typical models of reactors with gradually increased reaction spaces. b) Scale range of the different reactors.

To date, LoC systems have opened up a new concept and at the same time provided an attractive and highly efficient experimental platform for catalysis chemistry. However, there is still a lack of a review paper that summarizes the recent development in on-chip catalysis and synchronously pushes this dynamic field forward. In this paper, we would like to highlight this new concept and emphasize the importance of catalysis research based on microfluidics. The complementary relationship between catalysis and microfluidic devices is discussed briefly. Additionally, recent developments on new approaches to on-chip catalytic microreactors and their integration with multifunctional microfluidic devices are reviewed. Finally, the current challenges and future perspectives of this up-and-coming field are discussed based on our own opinions.

Need for On-Chip Catalytic Microreactors

Scale of catalytic reactors

The scale of a reactor plays a very important role in catalysis as scale-defined factors, which include mass and heat transfer, reactant mixing, and the probability of contact between the catalytic active sites and reactants, have a great influence on the catalytic process. To date, catalytic micro-nanoreactors with sizes that range from sub-nanometer to hundreds of microns have been successfully developed.[49–54]

A schematic illustration of typical reactors of various sizes is shown in Figure 1. Generally, the widely used zeolites are the smallest catalytic nanoreactors.[55,56] To some extent, the micropores of zeolites can be considered as molecular reactors, considering that the pore size of most zeolites is less than 1 nm. Similar to zeolites, metal–organic frameworks (MOFs) also possess sub-nanometer-sized nanoporous structures.[57] The voided porous structures contribute to a high surface area and confined reaction space, which leads to intimate contact with catalytic active sites and, therefore, high activity. However, the relatively small pore size prevents bulky molecules from entering the pores and blocks mass diffusion. To overcome these drawbacks, mesoporous materials have been prepared.[58] According to the IUPAC definition, a mesopore is in the range of 2–50 nm.[59] To date, typical mesoporous materials, such as MCM-41 and SBA-15, have been widely used in various catalytic reactions.[60] In most cases, these mesoporous materials act as catalyst supports, and the catalytic active sites are loaded by heteroatom doping, covalent grafting, or nanoparticle loading. In this regard, the mesopore channels could be considered

as nanoreactors. Compared with microporous materials, mesoporous structures provide larger pore volumes, which is of benefit to mass transfer. However, the amorphous nature of the pore walls results in relatively poor stability,[61,62] which limits their industrial applications. In addition to nanoporous materials, carbon nanotubes (CNTs)[63–67] and macroporous materials[68] prepared by hard-templating routes have also been used for catalytic reactions. As micro-nanoreactors, the diameters of CNTs are usually in the range of 1–100 nm, whereas the pore size of macroporous materials varies from tens of nanometers to several microns (Figure 1b). In addition to solo micro-/meso-/macroporous materials, hierarchical nanoporous structures have also been successfully prepared for catalysis with the features of high surface areas, facile mass transfer, and high stabilities.[51,53,69]

Over the past several decades, triggered by their high catalytic activities, catalysts based on micro-nanoporous materials have been developed. Various catalytic reactions inside the pores of nanoporous materials have been widely investigated. However, reactors with features that range in size from several to hundreds of microns have been paid less attention because most of the catalytic reactions have been performed in macroscopic instruments. Among catalytic reactors with different sizes, from molecular reactors (e.g., zeolites) to industrial reaction towers, investigations in the microfluidic range are relatively few. A possible reason for this omission is the relatively late development of microfluidic devices, which have been known since the mid-1990s. Nowadays, with the rapid progress of microfluidics in both chip-fabrication methodologies and multifunctional-component-integration techniques, on-chip catalytic microreactors face a bright future in modern catalysis research.

Microfluidics needs catalysts, catalysis needs microfluidic reactors

Briefly, the relationship between catalysts and microfluidic devices is complementary. With the rapid development of LoC devices, the manipulation of microfluid reactants is not limited to simple injection, reagent delivery, flow control, mixing, reaction, and analysis, and increasingly complex reactions are highly desired in microfluidic channels.[45,46,70–73] In this case, the presence of heterogeneous catalysts, for instance, solid acid/base, noble metals, metal oxides, and enzymes, inside microfluidic devices becomes important because they ensure the complete conversion of reactants. Moreover, the presence of catalysts would introduce additional functions to microfluidic devices. For instance, by using bimetallic catalysts, Ibele et al. successfully developed a microfluidic pumping system, and by using hydrazine derivatives as fuels, it is possible to control the direction of the microfluid flow in a system.[74] Recently, Zarzar et al. reported a straightforward procedure to integrate microscale Pt and Pd patterns, which could be used as catalysts to generate directed autonomous particle and fluid transport.[75] Catalysts will become necessary in the near future for microfluidic devices.

On the other hand, for catalysis, microfluidic devices provide a unique experimental platform. The advantages of microfluidic devices, which include low reagent consumption, high safety, facile mass/heat transfer, high surface-area-to-volume ratio, and high-throughput processing, endow on-chip catalytic reactors with various capabilities superior to macroscopic reaction settings. Firstly, the large number of parallel microchannels allow high-throughput catalytic reactions, which contribute to the feasibility of efficient catalyst screening.[76] Secondly, the high surface-area-to-volume ratio (ca. 10–500 times larger than that of conventional reactors) ensures not only a high mass/heat transfer rate but also intimate contact between catalysts and reactants, which, therefore, show much higher activities compared with those in general reactors. For example, Wilson and McCreedy fabricated an on-chip catalytic microreactor by dusting a thin layer of solid superacid (sulfated zirconia) onto the bottom of a microfluidic channel.[77] In this channel, the conversion efficiency of hexanol dehydration reached almost 100%, which is much higher than that observed in macroscopic reactors (ca. 30%). Furthermore, microfluidic reactors are amenable to be interfaced with other analytical instruments, which makes it possible to investigate catalytic reactions in situ. For instance, Xu et al. reported microfluidic chips decorated with Ag-microflower arrays, which could be used as a highly active catalytic reactor that allows the in situ monitoring of the catalytic reaction by using surface-enhanced Raman spectroscopy (SERS).[78] With the help of microfluidic devices, additional functionalities such as high-throughput catalyst assessment, investigation of catalytic mechanisms, monitoring catalytic reactions, screening of catalysts, and optimization of reaction conditions, could be realized in a safe, facile, and efficient manner.

New Approaches to On-Chip Catalytic Microreactors

Compared with conventional macroscopic reaction instruments, microfluidic reactors exhibit a series of unique features, such as enhanced control of reactants, trace material consumption, fast heat/mass transfer, high reaction rate, and low knockdown risk if the reaction runs out of control, which all benefit from the space confinement effect of microfluidic systems. The above mentioned advantages of microfluidic devices have stimulated the rapid progress of on-chip catalytic reactors. In recent years, various new approaches have been successfully developed for the fabrication of catalytic microfluidic reactors by immobilizing multiform catalysts such as noble metals, metal oxides, carbon, and enzymes onto microfluidic chips.

Initially, on-chip catalytic microreactors were simply fabricated by dusting a layer of catalyst powder inside a microfluidic chip. For instance, Wilson and McCreedy fabricated an acid-based microreactor by dusting a thin layer of sulfated zirconia powder on the surface of a microchannel, which could be used for on-chip heterogeneous catalysis.[77] In addition to the simple dusting of catalysts, Iles et al. reported the fabrication of microfluidic reactors with built-in metal catalysts by sputter-

ing catalytic metals into the channels of microfluidic reactors prior to device bonding.[79] This metal-catalyst-equipped on-chip reactor was later applied to the reduction of butyraldehyde to butanol and benzyl alcohol to benzaldehyde. Despite the successful realization of the loading of catalysts within microfluidic devices in these studies, on-chip catalysts still suffer from problems of poor stability and a low contact area with microfluidic reactants.

As an alternative approach, packed-bed catalytic reactors based on microfluidic devices have been successfully developed. In the packed-bed microreactor, microchemical systems can retain catalysts through channel design or with the help of filter units. Typically, packed-bed catalytic microreactors contain several parts, which include the inlet manifold for each reaction channel, a catalyst chamber that contains the catalytic particles, and the filter unit at the exit of the device, as well as a catalyst loading system to deliver the catalyst slurry to the reaction chamber. As a typical example, Losey et al. reported a microchemical device built of Si and glass by deep-reactive-ion etching technology, photolithography, and multiple wafer bonding for on-chip heterogeneous catalysis.[80] The microchemical system consisted of a microfluidic distribution manifold, a microchannel array, and a microfilter to immobilize activated carbon as the catalytic material in the reactor chip. In the hydrogenation of cyclohexene, the overall mass-transfer coefficients in this packed-bed microreactor were almost two orders of magnitude larger than the values reported for standard laboratory-scale reactors. In addition, Seong and Crooks designed and fabricated microfluidic channels with microbead-supported catalysts as on-chip reactors.[81] A microfluidic device based on polydimethylsiloxane (PDMS) has been fabricated by using standard photolithography followed by replica molding as shown in Figure 2. It consists of a Y-shaped inlet channel (100 μm in width, 23 μm in depth), a main channel that contains a weir, and ten detection lanes at the end of the main channel (50 μm in width, 23 μm in depth). Polystyrene microbeads with an average diameter of 15.5 μm were used to support enzyme catalysts. In this work, the packed microbead reactor not only provided abundant interstices that reduced the effective thickness of fluid laminae and, therefore, increased the fluid mixing rate (Figure 2) but also gave rise to a high surface area relative to that of the channel walls.

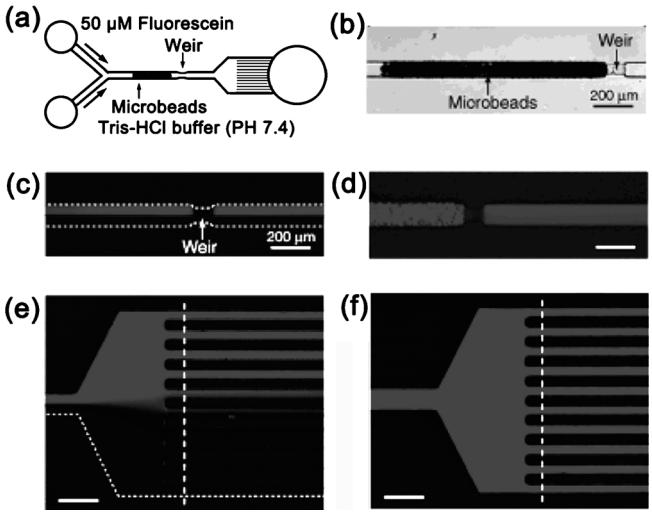

Figure 2. a) An illustration of the PDMS microdevice used to study two-stream mixing. b) Optical microscopic image of microbeads packed in the microreactor. Fluorescence micrographs of c) the open channel and d) the microbead-bed channel. e) Fluorescence micrograph of the 10-lane detection zone after the open channel. f) Fluorescence micrograph of the 10-lane detection zone after the microbead-containing channel. Adapted from Ref. [81]

In addition to liquid–solid heterogeneous catalysis, packed-bed microreactors also allow gas-phase reactions. Ajmera et al. reported the fabrication of a packed-bed reactor in Si for heterogeneous gas-phase catalyst testing.[82] The on-chip reactor consists of one inlet and one outlet for gas flow; the inlet channels bifurcate into 64 parallel channels that feed a wide catalyst bed, and an array of catalyst retainer posts acts as a filter to hold the bed in place. The catalyst is loaded into the reactor through the inlet port by using a vacuum placed at the outlet, which can generate the gas flow to fluidize the small catalyst particles and draw them into the reactor. In addition, the microreactor is reusable as the catalyst can be removed by applying a high pressure to the outlet, which blows the particles out of the inlet port. Park and Kim reported a dual-channel microreactor that allows gas–liquid syntheses.[83] The dual-channel microreactor consists of two microfluidic channels separated by a thin membrane. The gas and liquid reactants that flow in different microchannels can come into intimate contact because of the diffusion of gas into the liquid phase through the thin membrane (Figure 3), and the oxidative Heck reaction

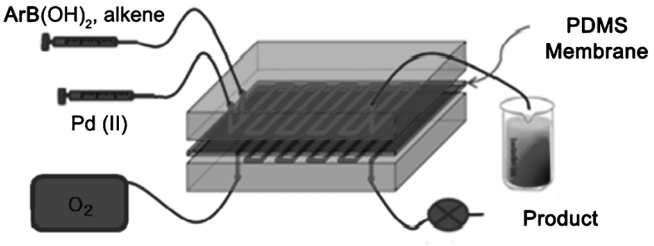

Figure 3. An illustration of the dual-channel microchemical system. Adapted from Ref. [83]

performed in the dual-channel microreactor showed significant improvements in terms of yield, selectivity, and reaction time. The new dual-channel microfluidic reactor allows independent control of the flow of the gaseous and liquid reagents, which provides a powerful tool to fully explore gas–liquid catalytic reactions.

As efficient catalysts, metal nanoparticles (NPs), for instance, Pt, Pd, and Au NPs, have been considered to be more active in a wide range of catalytic reactions relative to their bulk counterparts because of their high surface area and atom economy. For microfluidic reactors that use metal NPs as catalysts, the issue that should be solved initially is the immobilization of the NPs inside a microfluidic device. Lin et al. reported the in situ immobilization of Pd NPs inside a PDMS microfluidic re-

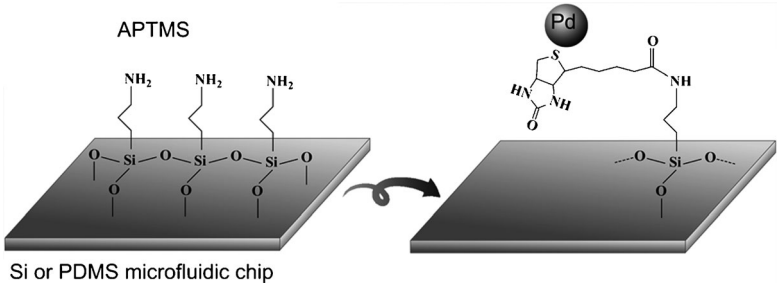

Figure 4. An illustration of the immobilization of biotinylated Pd NPs on Si or PDMS microfluidic reactors. Oxygen-plasma treatment leads to deposition of OH groups on the surface. The subsequent attachment of APTMS to the OH groups provides the amine groups required to immobilize the biotinylated Pd NPs on the surface. Adapted from Ref. [84]

actor through a covalent-grating route (Figure 4). Biotinylated Pd NPs with particle size in the range of 2–4 nm could be grated to the 3-aminopropyltrimethoxysilane (APTMS) modified PDMS channel.[84] In the hydrogenation of 6-bromo-1-hexene at room temperature under 1 atm of H_2 pressure, an average first-run conversion of 85% and selectivity of 100% were achieved. Jamal et al. first synthesized Au NPs in microfluidic systems and then immobilized them into fused silica capillaries that could be used as a catalytic microreactor.[85] Similarly, negatively charged Au NPs with an average size of 15 nm could be anchored to the silica surface by using aminopropyltriethoxysilane (APTES) as the coupling agent.

To further improve the intimate contact between catalysts and reactants inside a microfluidic reactor, catalyst NPs could be loaded onto high-surface-area carriers. For example, nanowires (NWs) could be used as a catalytic-material carrier for high efficiency microfluidic reactors. Kim et al. reported that highly stable diphenylalanine peptide NWs could be selectively self-assembled in the reaction zone of a microfluidic system.[86] After the hybridization of the Pd NPs, this system could be applied for microchemical hydrogenation and Suzuki coupling reactions. The NWs would give a surface area approximately 100 times larger than that of a flat surface, which significantly increases the amount of immobilized Pd NPs in the microchannel. At the same flow rate, the NW-embedded microreactor shows a much higher product yield than the plain microreactor. Later, the same group reported the fabrication of a macroporous-structure-embedded microfluidic system for on-chip catalysis.[87] In their work, 3D ordered macroporous polyfluoropolyether (PFPE) patterns were integrated into a microchannel by a series of porous-pattern-fabrication processes and subsequent photolithography in a site- and shape-selective manner. Pd NPs implanted on the surface of the macroporous structure were utilized as a catalytic microreactor to perform a Suzuki coupling reaction. These two examples provide a new and facile route for the fabrication of nanostructure-embedded microfluidic systems that may offer new applications in the area of heterogeneous catalysis.

Recently, with the rapid development of micro-nanofabrication techniques, a new laser processing technique has been adopted to functionalize microfluidic chips, which includes the integration of catalytic microreactors.[46,70,72,73,78] For example, the femtosecond laser direct writing (FsLDW) technique, which has been widely recognized as a powerful tool for the designable fabrication of 3D micro-nanostructures, has been successfully adopted for the integration of catalysts inside microfluidic chips.[78] A schematic illustration of the FsLDW system is shown in Figure 5a. The unique advantages of this system include designable processing features, widely processable materials (e.g., polymer, protein, metal, metal oxides, carbon, and hybrid

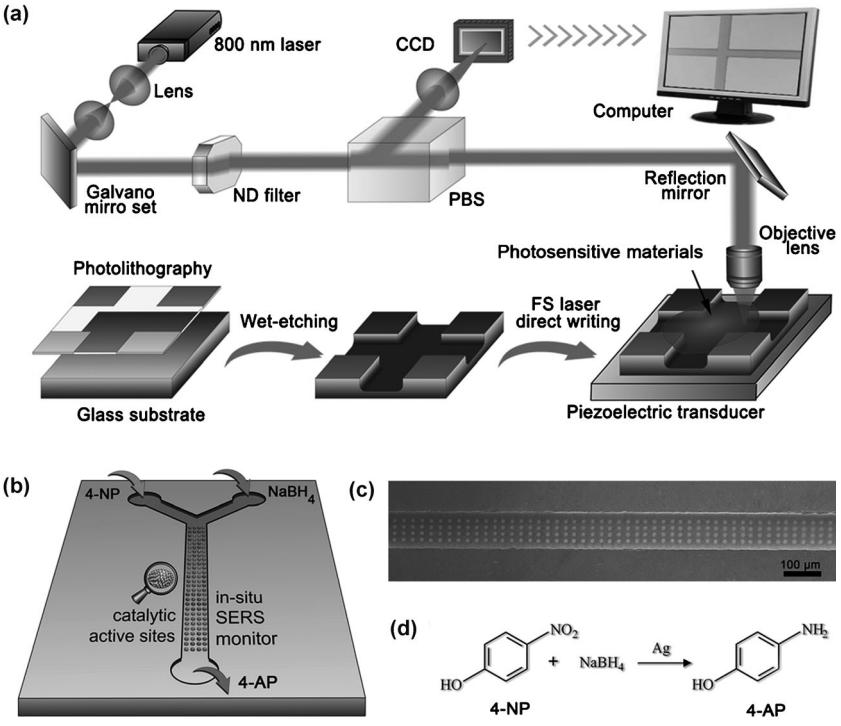

Figure 5. a) An illustration of the TPP-fabrication system used for the immobilization of catalytic materials inside a microfluidic chip. b) Schematic illustration of the Ag-microflower-equipped microreactor that could be used as an in situ SERS monitor. c) SEM image of the Ag-microflower-equipped microfluidic channel. d) The catalytic reaction. Adapted from Refs. [78, 93]

materials),[88–96] high spatial resolution, and accuracy, which make FsLDW an enabler for chip functionalization. By using FsLDW, we reported the on-chip fabrication of Ag-microflower arrays constructed by upright nanoplates and attached NPs as both catalytic active sites and an in situ SERS monitor for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) as shown in Figure 5b.[78] Notably, catalyst immobilization in this way benefits 1) the localized positioning of catalysts, 2) the high surface area of catalysts, 3) the uniform dispersion of catalytic active sites, and 4) stability against microfluid impingement. The laser-induced deposition of metal catalysts is not limited to Ag; Zarzar et al. have reported the integration of nanocrystalline Pt and Pd micropatterns by using precursors often used in platinotype/palladiotype photographic processes.[75] This noble-metal-catalyst pattern was later applied as a site-specific H_2O_2 decomposition catalyst, which can be used in the design and testing of catalytic micropumps and motors.

In addition to the general catalytic on-chip microreactor, microfluidic devices can be widely used in various biocatalytic reactions. Once a suitable strategy for the immobilization of biocatalysts, for example, enzymes and artificial enzymes, has been developed, a microfluidic bioreactor could be achieved accordingly. Similar to the grafting of metal NPs, a covalent-bonding method has also been used for enzyme immobilization inside microfluidic devices. In a typical procedure, microfluidic chips (e.g., Si, glass, or PDMS channels) are modified initially with special functional groups (e.g., organosilane), then enzyme molecules could be immobilized in the modified channel through a covalent-bonding process. In this way, Limbut et al. reported the fabrication and immobilization of urease onto a PDMS microchannel chip, which was used in a flow-injection conductimetric bioreactor to determine urea in real serum samples.[97] The urease immobilized on the microchannel chip by covalent bonding had a good stability (>30 days of operation) and good repeatability with a relative standard deviation (RSD) lower than 2.3%.

An enzyme-encapsulated sol–gel is another method used widely to create on-chip enzyme bioreactors. Its porous nature, large surface area, low fluorescent background, low nonspecific adsorption, and high capacity make the sol–gel a mild carrier for enzyme immobilization inside microfluidic channels. Sakai-Kato reported the fabrication of an on-chip bioreactor by the in situ gelatination of a trypsin-encapsulated sol–gel onto a polymethylmethacrylate (PMMA) microchip.[98] With the trypsin encapsulation, the sol–gel-equipped bioreactor integrates tryptic digestion, separation, and detection in a facile manner. Compared to conventional tryptic reaction schemes, this on-chip enzyme reactor shows high efficiency. Moreover, the encapsulated trypsin exhibits a much higher stability than that in solution. Zhan et al. reported a simple two-step method to fabricate poly(ethyleneglycol) (PEG) hydrogel-based microreactors within microfluidic channels.[99] The intrachannel micropatches could contain enzymes that are able to selectively catalyze specific reactions. Additionally, multiple micropatches that contain the same or different enzymes can be fabricated within a single channel. This strategy is considered to be sufficiently general to accommodate a number of catalytic and synthetic applications. Microfluidic chips play a very important role in on-chip bioreactors because the spatial confinement of the microfluidic channel would not only facilitate the immobilization of biocatalysts (e.g., enzymes and their mimics) but also improve contact with the reactants.

Integration of Catalytic Microreactors with Multifunctional Microfluidic Devices

Initially, microfluidic devices generally consisted of only simple microchannel networks and reactant inlet/outlet reservoirs. Experimental handling, which includes sample mixing, reagent supply, reaction control, and product separation, is accomplished by manipulating the microfluids. Simple microfluidic devices are competent for general analysis; however, they are still incapable of controlling complex catalytic reactions. To date, with the rapid progress of chip fabrication and functionalization techniques, an increasing number of functional units could be integrated into channels to serve as a filter, temperature controller, SERS monitor, mixer, pump, and even transporter.[46,70–73,75,93] The integration of multifunctional devices with microfluidic chips not only provides various components to achieve the desired reaction conditions but also shows strong technique support and hardware security for high-efficiency catalytic microreactors. In the following paragraphs, we will give some representative examples.

A microfilter has been introduced as a major compartment in a packed-bed catalytic microreactor to retain catalytic particles such as microbeads and microparticles. By using a two-photon-photopolymerization (TPP) technique, Wang et al. successfully fabricated a series of polymer microsieves with round-, square-, rounded-end- rectangle-, pentagram-, and equilateral-triangle-shaped pores and adjustable pore sizes in the range of 3.5–6.0 μm perpendicular to the microfluidic channel.[72] Additionally, through the design and fabrication of a fish-scale-like microstructure (eave-covered pores), the microsieves could serve as a one-way valve to separate the solid microparticles from liquids. The flexible integration of microsieves with variable pore size, shape, and position holds great promise for catalyst loading in the development of catalytic microreactors.

Temperature control is very important for on-chip catalytic reactions. Recently, various thermal devices have been successfully integrated into microfluidic systems, which include both contact heating methods, such as an electric heater, a Peltier semiconductor heater/cooler, a surface-film resistor heater/sensor, and noncontact heating methods, such as IR and plasmon heating. For instance, Sun and Gillis reported an opaque indium tin oxide (ITO) film as a resistor heater, which is compatible with optical detection.[100] Lao et al. deposited a 10 nm Ti film and a 100 nm Pt film as both heater and temperature sensor on the surface of a 400 μm Si chip. Mao et al.[101] demonstrated a microfluidic device with a linear temperature gradient, in which an array of microfluidic channels sits between a hot source on the left and a cold sink on the right.[101] Xu et al. reported the integration of a localized Ag heater through the multiphoton-absorption-induced photoreduction of a Ag precursor.[94]

To increase the mixing efficiency of reagents, a mixer is essential for microfluidic systems. Generally, there are two main mixing methods in microfluidic systems, the first is passive mixing, which needs a complex design of 3D structures or a long mixing channel, and the second is active mixing, which is more effective in a short mixing length but needs an external power supply. As representative examples, Lim et al. reported a neoconceptive passive 3D crossing manifold mixer (CMM) embedded in a microchannel fabricated by using TPP lithography.[102] The CMM has a configuration of layered crossing tubes that guide and realign fluids effectively, and the almost complete mixing (90% efficiency) of ethanol with a fluorescent dye and water was achieved in a channel length of 250 μm. Tian et al. reported the fabrication of a magnetic microturbine by using the FsLDW technique and illustrated the use of this remotely controlled turbine as an active mixer in microfluidic mixing.[70]

In addition to the above mentioned microdevices, a micropump to control fluid flow has been developed. To date, mechanical pumps (e.g., electromagnetic pumps, static-electric pumps, hot gas power pumps, piezoelectric pumps, and atmospheric-pressure pumps) and nonmechanical pumps, such as electro-osmosis, magneto-hydrodynamics (MHD), electro-hydrodynamics (EHD), and capillary action have been developed. In addition, to make the microfluidic devices amenable to be interfaced with various analytical instruments, necessary microcomponents have been fabricated, of which SERS substrates are typical examples. Lee et al. demonstrated an on-chip SERS monitor that was constructed from a robust Ag nanowell.[103] Xu et al. fabricated a SERS-active microfluidic channel with tunable surface-plasmon resonances by coating a Ag layer on grating-embedded microchannels.[45] By using the FsLDW technique, they also reported the in situ fabrication of Ag-patterned SERS substrates, which allowed the real-time detection of analytes during chemical reactions and demonstrated the feasibility of detection in different reaction areas.[46] With the development of micro-nanofabrication techniques, functional devices and structures could be readily created inside microfluidic devices, and the integration of new multifunctional components would greatly enhance the capability of microfluidic chips in various applications, especially for on-chip catalysis.

Current Challenges and Future Perspectives

At present, although microfluidic catalysis started more than ten years ago, the on-chip catalytic microreactor is still at an early stage. A possible reason for this is the lack of advanced micro-nanofabrication technologies that can be used for the fabrication of microfluidic devices equipped with various catalysts. With the rapid development of new microprocessing techniques for chip preparation and multifunctionalization, LoC systems have progressed over the past two decades. In this regard, it is time to bring the concept of on-chip catalysis to the modern catalysis research.

Through a review of the existing work in this dynamic field, it can be concluded that the main challenge for the development of catalytic microfluidic reactors is the loading of various catalysts in the microfluidic devices available currently. In principle, silica-based microfluidic chips, which include glass, Si, and quartz, could be used for catalytic reactions in organic solvents or at high temperature because these inorganic chips have relatively high stabilities. On the contrary, polymer-based microfluidic chips, such as PMMA and PDMS, would be suitable for water-phase catalysis, for instance, bioreactions. The immobilization of catalysts on these microfluidic devices may be different for different microchannels. In addition, the challenge also lies in the solution to problems that include the quantitative loading of catalysts, controllable positioning of catalysts, uniform dispersion of catalytic active sites, high surface-area-to-volume ratio of catalysts, and superior stability. To date, although new catalyst-immobilization approaches, which include catalyst-powder dusting, sputtering, packed-bed encapsulation, filter membrane, high-surface-area supports, covalent grafting, sol–gel supports, and laser processing, have been successfully developed, there is still an urgent call for a generally applicable method to load various catalysts inside microfluidic devices.

However, to ensure that diverse reaction conditions could be realized inside the microfluidic chips, functional components should be integrated with on-chip catalytic microreactors. This may depend on the state-of-the-art of micro-nanofabrication techniques, the innovation of new functional materials and structures, and supporting instruments for microfluidic devices. With the gradual development of microfluidics, all of the required functional components that are used for experimental handling would be integrated with LoC devices, and the microfluidic reactor would act as a highly efficient experimental platform for future catalysis research.

Conclusions

Compared with macroscopic reactors, microfluidic systems have many merits, which include low reactant consumption, environmental friendliness, high safety, high efficiency, high sensitivity, and portability. In particular, for catalysis investigation, microfluidic reactors provide a confined reaction space that benefits mass/heat transfer, which leads to high reaction rates and activities. These unique advantages of microfluidics constantly stimulate the development of on-chip catalytic reactors. To date, many new approaches have been successfully adopted for both the fabrication of microfluidic reactors and on-chip catalytic testing; and the reported results show that microfluidic catalytic reactors show a better performance, such as high yield, short reaction time, easy handling, high throughput, and low consumption, than macroscopic instruments. Consequently, it is clear that microfluidic reactors can be considered as highly efficient experimental platforms for various catalytic reactions. With the rapid progress of microfluidics, on-chip reactors could become a popular method for catalysis research in the near future.

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