Research Highlights

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Nanoparticle synthesis in microdroplets

During the past couple of years a number of reports have described the use of continuous flow, microfluidic devices for the direct synthesis of metal, metal-oxide, compound semiconductor and organic nanoparticles. The primary benefit of such approaches lies in the exquisite control of reaction parameters that accompanies system downsizing. Parameters such as relative reagent concentrations, temperature, pressure and reaction residence times can be maintained with great precision or be varied in a rapid and controllable manner should it be desired.

Nanocrystalline colloidal semiconductors have tuneable optical and electronic properties and therefore their use in electronic devices and optical biosensing is of high current interest. The physical characteristics of these nanocrystallites are determined primarily by spatial confinement effects with the optical band gap often differing considerably from the bulk semiconductor. As these properties are ultimately determined by the physical dimensions of the crystallites, the ability to synthesise nanoparticles of well defined size and shape is requisite. In reality, deviations about the mean particle radius should be lower than one percent. Unfortunately, this is beyond the tolerance of most standard 'bottom up' synthetic routes and in general it is necessary to employ some form of post-treatment to extract the desired particle size and sample size distribution. Using such post-hoc approaches, it is possible to obtain nanoparticles with extremely narrow size distributions, however processing can be complex and yields are generally low. Accordingly, it is preferable to use direct techniques, requiring no post-treatment, to prepare the crystals. Although continuous flow microfluidic reactors have demonstrated much promise in improving particle size and size-distribution control, the use of hydrodynamic flow motivation (which is ideal when using common solvent systems) does lead to inherent broadening of particle size distributions (under typical conditions) due to unavoidable residence time distributions. Interestingly, it has been shown that segmented-flow microfluidic systems can be useful in reducing these dispersion effects to generate particle populations of well-defined size and shape. New developments in this area have recently been reported by Richard Mathies and co-workers at the University of California at Berkeley.[1] In these studies the authors demonstrate the fabrication and operation of microfluidic droplet reactors which can be used for high-temperature synthesis of CdSe nanoparticles.

Specifically, the authors utilise a stepped microstructure to controllably and rapidly generate octadecene droplets flowing within a perfluorinated carrier fluid. A nanojet injector combined with an expansion step (in channel height) is used for efficient droplet formation at high capillary numbers. This in turn means that droplets can be maintained and manipulated with high efficiency at the high temperatures (240–300 °C) necessary for efficient transformation. The microfluidic devices are fabricated in glass using standard lithographic protocols, and as can be seen in Fig. 1, incorporate a step increase in channel height from 45 to 90 μm downstream of the injection cross. To generate stable droplet flow, the authors silanize microchannel surfaces to allow preferential surface wetting by the continuous (perfluorinated polyether) phase. Using this approach, CdSe nanoparticles are successfully synthesised in droplets of octadecene within a continuous perfluorinated carrier. Importantly, the use of nL-sized droplets to contain reagents prevents both particle deposition and hydrodynamic dispersion and thus allows the production of high-quality nanoparticles with reduced polydispersity. Furthermore, the use of optical detection techniques allows each droplet to be interrogated and screened on-line and in real time. In general, these elegant studies demonstrate that nanoparticle synthesis can be performed in a rapid and controllable manner within droplet streams both at high temperatures and high capillary numbers. Although the methods have been applied to the synthesis of CdSe nanoparticles, such an approach will undoubtedly prove useful in synthesising a wide variety of high-quality nanocrystallite materials.

Addressable microfluidic patterning

In recent years microfluidic systems have been used as efficient tools in patterning and growing materials on planar surfaces. Although such approaches can be straightforward to implement, their application has typically been confined to relatively simple patterning applications. Although programmable and configurable patterning of complex

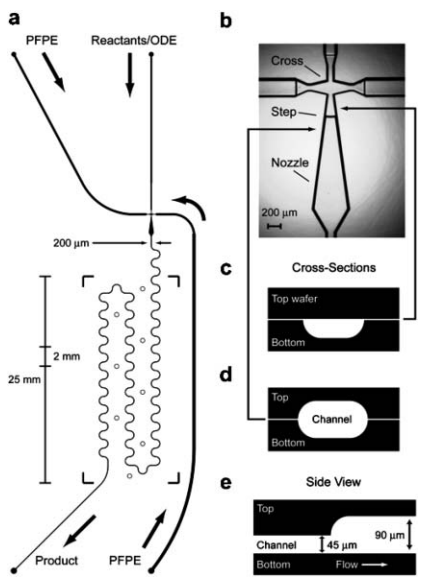

Fig. 1 Microfluidic droplet reactor. (a) Channel schematic. (b) Optical micrograph of droplet injection cross. Octadecene is injected in the top channel, while the PFPE is injected in the side channels. The narrowest point is 160 m wide. (c) Lateral "D"-shaped cross-section of channel etched on the bottom wafer only. (d) Cross-section of ellipsoidal channel etched on both top and bottom wafers. (e) Axial cross-section showing the 45 m step up in channel height. (Adapted with permission. Copyright 2005, The American Chemical Society.)

structures can be achieved, this normally entails the fabrication and use of sophisticated and costly microfluidic tools. To this end, Jau-Ye Shiu and Pelin Chen at the Academia Sinica in Taiwan have recently reported a simple approach for addressable microfluidic patterning which allows fluids to be manipulated with high-precision using soft lithography and the electrocapillary effect.[2] In a basic sense, programmable patterning is facilitated through the creation of valves and pumps which can be operated in tandem to move and confine fluid to a specific region. In the current studies the authors use the electrocapillary effect to achieve both functions. Application of an electric field between a conductive solution and an electrode leads to variations in interfacial tension, which in turn generates pressure. Importantly, if the electrode is isolated from the fluid medium ohmic heating and electrochemical reactions are prevented.

In the described experiments, the authors use two sets of electrodes (row and column electrodes) to provide for fluid pumping and localisation (or valving). Microfluidic structures are produced by replica moulding of PDMS and consist of microchannels for fluidic manipulation and chambers for fluidic containment. Electrode arrays are fabricated by etching ITO coated glass slides, and are electrically isolated from the microchannels using a 10 μm thick layer of PDMS. Using this simple approach fluid can be precisely manoeuvred and delivered to microchambers at linear velocities of up to 75 μm s^{-1}. Importantly, the authors demonstrate addressability by patterning a variety of fluidic media (including phosphate buffered saline solution and protein solutions) using simple electrode control routines (Fig. 2b and 2c) and also growing yeast cells within defined microchambers (Fig. 2d). The ability to pattern biological samples in two dimensions with high precision and control clearly offers much potential when designing biological screens and sensor systems, and lifetime studies suggest that the described devices can be reused multiple times with no observed performance reductions. Moreover, the simplicity of the approach suggests that higher density electrode-channel arrays should be easily achievable, thus allowing more complex biological analyses to be performed in a similar manner.

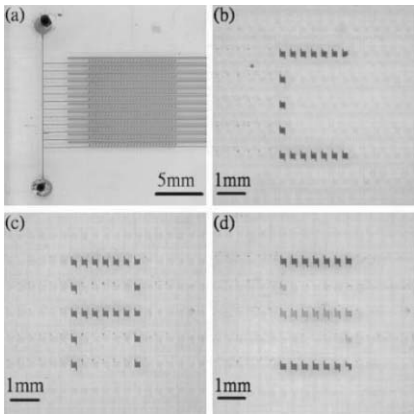

Fig. 2 (a) Image of 12 × 28 microfluidic chamber array (chamber dimensions: 200 μm × 200 μm × 30 μm). (b) Letter 'C' written by PBS dye solution. (c) Letter 'A' formed by patterning BSA solution with Coomassie blue. (d) Letter 'S' composed of four different tissue marking dyes in LB Broth. (Adapted with permission. Copyright 2005, Wiley-VCH.)

Microfluidic interfacial tensiometry

Interfacial tension (σ) measures the surface free energy that exists between two immiscible liquid phases or the molecular attractive force between unlike molecules at the interface. It is an important quantity, since the performance of detergents and reaction media can critically depend on σ. For example, the energy barrier produced by interfacial tension prevents one liquid from becoming emulsified into the other. Moreover, within microfluidic systems interfacial tension normally dominates gravitational and inertia forces. Consequently, the ability to accurately determine σ is desirable. To this end, Steven Hudson and colleagues at the National Institute of Standards and Technology in Gaithersburg have proposed and demonstrated a simple microfluidic device to accurately measure σ for a variety of fluidic systems.[3] In basic terms their approach involves both forming and then deforming drops (by extensional flow) within a two-phase system. Droplets are formed at a junction between immiscible streams and then can be deformed downstream by introducing flow constrictions in the microfluidic channel which generate extensional flow gradients. Simply, a converging channel will accelerate flow whilst a diverging channel will cause flow deceleration. The authors can then assess droplet deformation and extension rates by imaging droplet shape and position in real time using bright field optical microscopy.

Microfluidic devices are fabricated using a thiolene frontal photopolymerisation technique developed previously within the group or by SU8 photolithography. Using these methods PDMS devices can be created, and sealed to glass flats using an oxygen plasma. Using this approach, the authors are able to measure σ for a variety of immiscible fluid combinations. Data compare well with literature values and the system is shown to perform over a wide range of σ (2.5–60 mN m^{-1}). The authors expect that an increase in range can be achieved through operation at lower volumetric flow rates and by utilising an image acquisition camera with a higher frame rate. Importantly, high accuracy measurements can be performed within seconds whilst utilising minimal volumes of reagent.

Microfluidic interfaces review

A forthcoming review article by Javier Atencia and David Beebe at the University of Wisconsin Madison describes the role of interfacial phenomena within microfluidic system development.[4] The article provides a concise and interesting summary of some of the important developments in the field which utilise the unique properties of fluid flow on the microscale. Key discussions include the importance of viscosity rather than inertia when operating within microfluidic environments, and how interfacial phenomena may be harnessed and controlled to generate novel systems for chemical and biological analysis. Application areas that are discussed and critiqued include controlled droplet formation, surface patterning and pinned interfaces for immiscible fluids, and the exploitation of interfacial phenomena in miscible flowing systems.

Mouldless fabrication of cylindrical microchannels

Standard lithographic and wet-etching techniques have traditionally been used

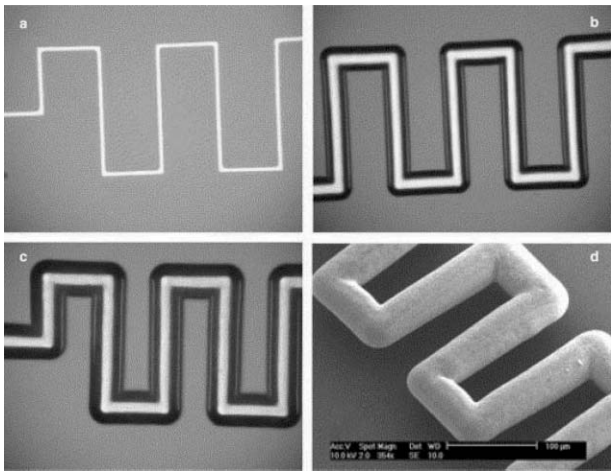

Fig. 3 (a) 5 μm wide metal seed pattern, (b) copper growth after 30 min of electroplating (feature height ~30 μm), (c) copper growth after 55 min of electroplating (feature height ~50 μm), (d) SEM image of cross-section of 50 μm-replication master structure. (Adapted with permission. Copyright 2005, Elsevier B.V.)

to structure microchannels in glass substrates. Such methods are well-developed and used to create microfluidic devices for a diversity of applications. One of the primary drawbacks associated with standard wet-etching methods is the isotropic nature of the etching process, which results in channels with trapezoidal cross-section and low aspect ratios. Soft lithographic methods for the structuring of elastomeric materials have become popular over the past few years as a rapid, flexible and low-cost route to the creation of micron-sized features on planar substrates. In many instances, such structures are created by replica moulding using negative masters made from structured photoresist layers. In this situation, resulting channels may have rectangular cross-sections and larger aspect ratios. Although useful, masters made from photoresist are not robust and cannot be used indefinitely for replica fabrication.

A nice development in this area has been described recently by Je-Kyun Park and associates at the Korean Advanced Institute of Science and Technology.[5] The authors report the use of a mouldless electroplating technique for fabricating cylindrical microchannels. In brief, conventional lithography is used to create a 5 μm wide gold strip on a glass substrate. This strip can then act as a seed layer in a subsequent electroplating process, and allows the electrochemical growth of a semicylindrical copper pole (Fig. 3b and 3c). This structure can then be used as a master off which elastomeric structures may be cast. In this way channels with circular or semi-circular cross-sections may be fabricated with ease (Fig. 3d). Significantly, the electrochemical growth of the copper pole can be controlled to vary channel dimensions and the resulting master structure can be used repeatedly with little degradation in surface properties.

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