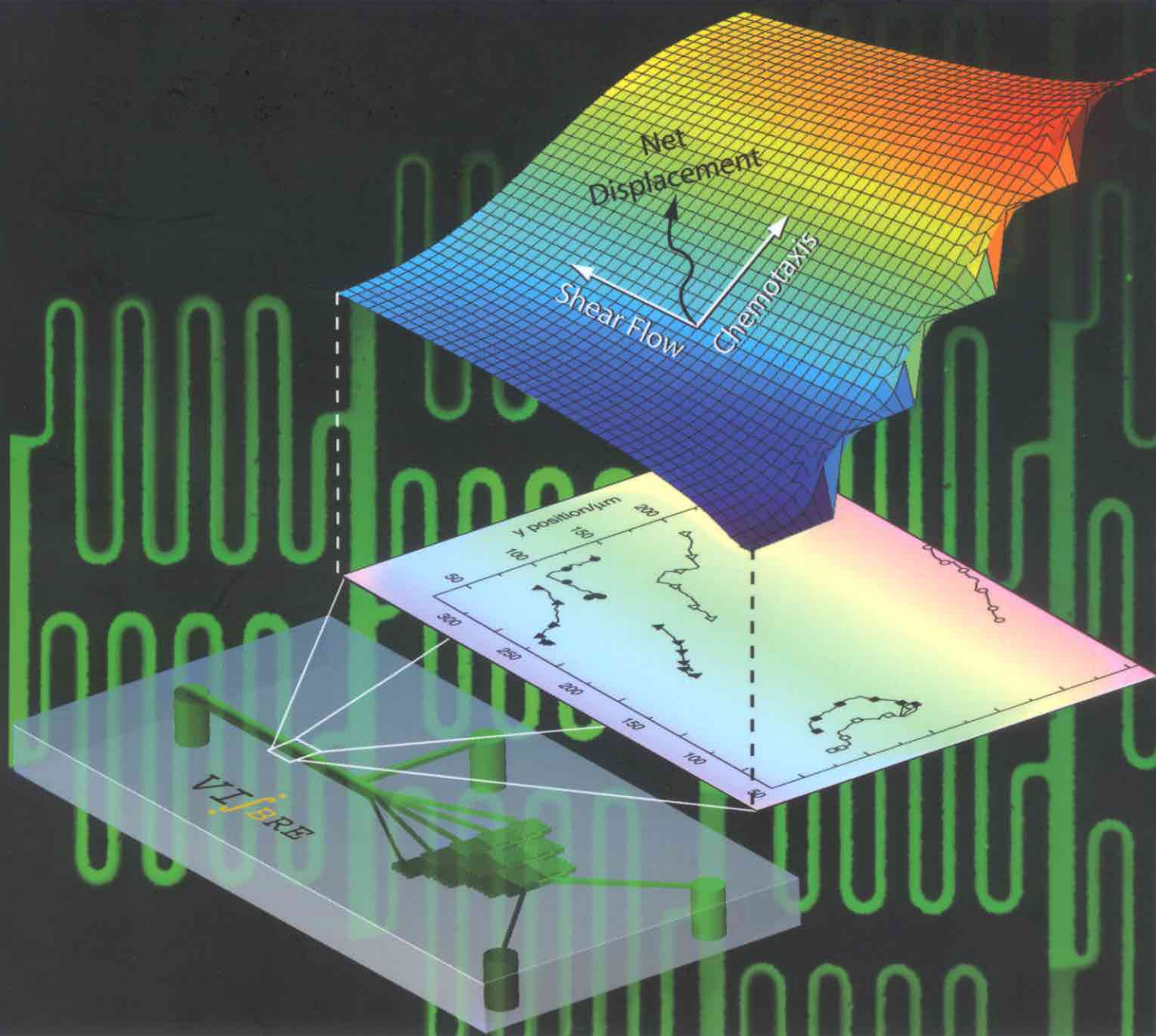


Lab on a Chip

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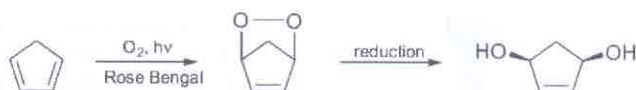
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Scheme 1

of a falling-film reactor for the photooxygenation of olefins.

Specifically the authors investigate the photooxygenation of cyclopentadiene using singlet oxygen and Rose Bengal as a photosensitiser (Scheme 1) to generate 2-cyclopenten-1,4-diol. The falling-film reactor is used to generate thin-liquid layers (which aid improved heat and mass transfer) through the use of 32 parallel microchannels (each 66 mm long, 600 microns wide and 300 microns deep). As the liquid reactants fall downwards they are contacted with an oxygen flow and the entire mixture irradiated using a xenon lamp. With active cooling of the system the authors demonstrate an overall product yield of 20%. Although no data relating to volumetric throughput is discussed, such a microscale approach should in the future allow efficient photochemical conversions to be performed on a preparative scale.

Chem. Eng. Technol., 2005, **28**, 427.

Core-shell nanoparticle synthesis

Over the past couple of years a number of literature reports have illustrated the utility of continuous-flow microfluidic systems in the synthesis of metal, metal oxide and compound semiconductor nanoparticles (see *Microscale Reactors: Nanoscale Products*, *Lab Chip*, 2004, **4**, 11N). Such studies have clearly demonstrated that microfluidic systems allow experimental variables such as temperature, flow rate, reagent concentration and residence times to be varied and controlled in a rapid, reproducible and precise manner. This directly leads to nanoscale products whose size and size distributions (and therefore optical and electronic properties) can be tuned to a particular application.

A material which has been extensively studied and characterised over the past decade is cadmium selenide. Light emission in CdSe quantum dots is of particular interest due to the strong dependency of emission wavelength on particle size. In simple terms, emission

can be tuned across the entire visible region of the electromagnetic spectrum by changing the mean diameter of the nanoparticle. This, combined with high photoluminescence quantum efficiencies and low photodegradation rate coefficients makes CdSe potentially useful in biological sensing applications. To maximise light emission from CdSe nanoparticles deposition of surface capping agents such as ZnS or CdS is commonly used to increase fluorescence quantum efficiencies. Although this approach has been shown to be highly successful, the ability to tune the characteristics of the capping layer and optimise emission properties is often synthetically challenging, time-consuming and ill-defined. Progress towards alternative processing routes has recently been reported by Hideaki Maeda and associates at the National Institute of Advanced Industrial Science in Japan. In these studies the authors describe the use of simple capillary reactors for synthesizing highly luminescent core/shell CdSe/ZnS nanoparticles.

In initial studies the authors demonstrate efficient synthesis of ZnS nanoparticles from diethyldithiocarbamic acid zinc salt in trioctylphosphine within a 200 μm diameter capillary. At a reaction temperature of 240 $^{\circ}\text{C}$ thermolysis to form ZnS nanoparticles is rapid and efficient, with UV absorption spectra and X-ray diffraction measurements confirming the presence of cubic ZnS nanoparticles 1.8 nm in diameter. To demonstrate controlled formation of core/shell nanoparticles the authors then use a series of previously produced trioctylphosphine oxide-capped CdSe nanoparticles (with sizes varying from 2.8 to 4.9 nm). These CdSe nanoparticles are mixed with an equal volume of the zinc-acid precursor in TOP, and injected into a reaction capillary at 240 $^{\circ}\text{C}$. Spectroscopic analysis of chip effluent indicates the successful formation of ZnS-capped CdSe nanoparticles at a variety of flow rates, with an optimum ZnS layer thickness (and thus highest fluorescence quantum efficiency)

for average residence times between 14 and 28 seconds. For residence times in excess of 28 seconds, the photoluminescence gradually decreases. Moreover, the FWHM of the luminescence peaks increases by up to 20 nm, and a pronounced red-shift is observed. This behaviour has been reported in previous studies, and is attributed to either the partial leakage of the exciton into the ZnS lattice, or possible merging of electronic energy levels due to increased size and lattice mismatch between the CdSe and ZnS crystal structure.

Further studies were repeated for an octadecene/trioctylphosphine system, with the initial CdSe nanocrystals being passivated by ODE rather than TOPO. Similar results were observed with reports of core/shell nanoparticles having fluorescence quantum efficiencies as high as 70%. Significantly, efficient synthesis is achieved at temperatures between 150 and 180 $^{\circ}\text{C}$, with average residence times less than 60 seconds. In comparison batch reactions (using identical CdSe nanocrystal precursors) take 40 minutes and generate particles with fluorescence quantum efficiencies of approximately 20%, indicating slow heating rates and poor control of reagent addition. To round off these studies the authors also show that the ZnS capped CdSe nanoparticles can be coated with 11-mercaptopundecanoic acid to render them water soluble, with minimal reductions in fluorescence quantum yield.

Adv. Funct. Mater., 2005, **15**, ASAP Article (DOI: 10.1002/adfm.200400164).

Direct-write assembly of three-dimensional microvascular networks

The evolution of increasingly complex microfluidic systems has been successful in extending their application to a diversity of chemical, biological and mathematical problems. Existing approaches for the creation of three-dimensional microfluidic devices often involve the use of convoluted and experimentally complex fabrication protocols. For example, the simplest route to multi-layer structures involves alignment and subsequent stacking of prefabricated two-dimensional structures. Although successful such methods are time-consuming, rely on precise alignment

between fluidic layers and are only applicable to relatively simple networks. Recent developments in soft-lithographic techniques have to some extent allowed more straightforward routes to the fabrication of complex, multilayer fluidic structures; however these techniques are typically confined to relatively thin device architectures and constrained by limited substrate materials. To this end, Scott White, Jennifer Lewis and colleagues at the University of Illinois at Urbana-Champaign and the École Polytechnique de Montréal have recently described an innovative method of assembling complex three-dimensional microvascular networks with interconnecting microchannels for analytical applications. In their most recent research, the authors report the development of a new fugitive ink that enables the direct-write assembly of scaffolds containing more than one hundred fluidic layers.

The basic process for fabricating these three-dimensional microvascular networks is shown in Fig. 2. Fabrication begins with the deposition of the fugitive ink through a cylindrical nozzle onto a moving x - y platform yielding a two dimensional pattern (Fig. 2(a)). The ink exits the nozzle as a continuous, rod-like filament and is directly deposited onto a moving platform. Once a layer is generated, the stage is raised by a defined amount and rotated, and another layer is deposited in the same manner. This process is repeated until the desired scaffold is produced (Fig. 2(b)). Next, the scaffold structure is surrounded and infiltrated with an epoxy resin (Fig. 2(c)). The resin is allowed to cure and solidify, and then the construct is heated to melt away the waxy ink and leave behind a network of interconnecting microchannels (Fig. 2(d) and (e)).

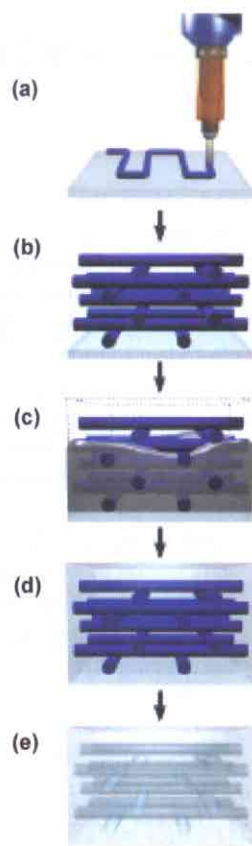


Fig. 2 Schematic representation of the fabrication of 3D microvascular networks by direct-write assembly: (a) deposition of fugitive ink; (b) multilayer scaffold after ink deposition; (c) resin infiltration into scaffold; (d) resin solidification to form structural matrix; (e) three-dimensional microvascular network created after ink removal. (Adapted with permission. Copyright 2005, WILEY-VCH Verlag GmbH & Co. kGAA.)

Successful processing critically relies on the several physical and chemical properties of the ink. The ink must flow through the deposition nozzle under high shear whilst being self-supporting. In addition, it must maintain shape and structure during resin infiltration and must liquefy at moderate temperatures

to ensure facile removal during the final phase. To meet the above requirements the authors have developed a fugitive ink comprising of a binary mixture of microcrystalline wax and a lower molecular weight organic phase with tailored mechanical properties. The optimal ink composition for direct writing was determined to be 40 wt.% microcrystalline wax. This ink makeup provides a good compromise between adequate stiffness for self-supporting behaviour and a moderate shear yield stress for facile manipulation through the deposition nozzle.

The new fugitive ink formulation extends capability of creating three-dimensional microvascular networks *via* direct-write assembly and allows the ambient deposition of scaffolds with high aspect ratios and device complexities. These developments open new avenues for microfluidic systems in a broad range of technological applications such as chaotic mixers, autonomic heating materials and self-cooling polymer structures. To demonstrate the efficacy of such structures in fluidic mixing applications the authors fabricate a microdevice consisting of 32 layers of interconnected microchannels (200 microns in diameter) in an epoxy matrix. A photocurable resin is then delivered into the network and spatially defined UV exposure used to create spiral 'mixing towers'. Testing of such devices indicates significant enhancements in fluidic mixing when compared to two-dimensional microchannel networks. In conclusion, the use of these high-quality fugitive inks for direct-write fabrication of microfluidic structures will undoubtedly aid the creation of highly complex fluidic networks and engender a diversity of new technological applications.

Adv. Mater., 2005, **17**, 395.

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