Ceramic microparticles and capsules via microfluidic processing of a preceramic polymer

Congwang Ye¹, Anthony Chen², Paolo Colombo^{3,4,*}
and Carlos Martinez¹

¹*School of Materials Engineering, Purdue University, West Lafayette, IN, USA*

²*Imperial College, London SW7 2AZ, UK*

³*Dipartimento di Ingegneria Meccanica, Settore Materiali Università di Padova, Padova, Italy*

⁴*Department of Materials Science and Engineering, The Pennsylvania State University, University Park 16801, PA, USA*

We have developed a robust technique to fabricate monodispersed solid and porous ceramic particles and capsules from single and double emulsion drops composed of silsesquioxane preceramic polymer. A microcapillary microfluidic device was used to generate the monodispersed drops. In this device, two round capillaries are aligned facing each other inside a square capillary. Three fluids are needed to generate the double emulsions. The inner fluid, which flows through the input capillary, and the middle fluid, which flows through the void space between the square and inner fluid capillaries, form a coaxial co-flow in a direction that is opposite to the flow of the outer fluid. As the three fluids are forced through the exit capillary, the inner and middle fluids break into monodispersed double emulsion drops in a single-step process, at rates of up to 2000 drops s⁻¹. Once the drops are generated, the silsesquioxane is cross-linked in solution and the cross-linked particles are dried and pyrolysed in an inert atmosphere to form oxycarbide glass particles. Particles with diameters ranging from 30 to 180 µm, shell thicknesses ranging from 10 to 50 µm and shell pore diameters ranging from 1 to 10 µm were easily prepared by changing fluid flow rates, device dimensions and fluid composition. The produced particles and capsules can be used in their polymeric state or pyrolysed to ceramic. This technique can be extended to other preceramic polymers and can be used to generate unique core-shell multimaterial particles.

Keywords: ceramic; microfluidic; capsule

1. INTRODUCTION

The synthesis and fabrication of particles and capsules with tailored microstructures have received significant attention in the last 15 years owing to their potential applications in drug delivery, electronic displays and biotechnology. There has been a fundamental transition in viewing particles as material feedstock for the fabrication of large objects to individual units with their own form and function. The driving force for this transformation is the development of new processing techniques to fabricate these materials with enhanced properties, such as high surface area, narrow particle size distribution, total porosity, shell thickness and permeability. In many advanced applications such as drug and gene delivery, photonics and catalysis, the distribution and organization of matter play an important role in providing new functionalities. Development of

new fabrication methods for new and old materials is essential to the growth in this area.

A myriad of methods have been developed to fabricate particles and capsules with controlled properties and they can be divided into several groups based on: hard and soft colloidal templating (Xu & Asher 2004), layer-by-layer deposition (Caruso *et al.* 1998), template-free synthesis (Lou *et al.* 2006a) and more recently microfluidics (Nie *et al.* 2005, 2006), particle-stabilized emulsions (Akartuna *et al.* 2009) and electrohydrodynamic spraying (Nangrejo *et al.* 2008). Innovative particles and capsules have been developed with these techniques, including SnO₂ nanoparticle microshells for sensing (Martinez *et al.* 2005), silica hollow spheres and microballons (Zoldesi & Imhof 2005), silica nanocages (Lou *et al.* 2006b), polystyrene colloidosomes with selective permeability (Dinsmore *et al.* 2002) and gold nanocages as optical image contrast enhancers (Chen *et al.* 2005).

Microfluidics has emerged as a powerful and flexible technique to fabricate tailored particles and capsules. Polydimethylsiloxane (PDMS)/glass devices with

*Author for correspondence (paolo.colombo@unipd.it).

One contribution to a Theme Supplement 'Scaling the heights—challenges in medical materials: an issue in honour of William Bonfield, Part I. Particles and drug delivery'.

T-junction channels have been used to generate hydrogels (Kim *et al.* 2007), polymeric capsules (Nie *et al.* 2005), silica granules (Shepherd *et al.* 2006) and colloidosome structures (Shah *et al.* 2010). Their low cost and flexible design have made them an important tool in particle fabrication. However, the use of PDMS prevents the use of either strong solvents or siloxane-based compounds since they deteriorate the PDMS microstructure. Moreover, it is difficult to selectively coat adjacent channels in a device to enable the formation of double emulsion drops often necessary to produce capsules (Okushima *et al.* 2004). Utada *et al.* (2005) recently introduced a new class of microfluidic devices based on the coaxial arrangement of glass capillaries. These devices overcome the two limitations of the PDMS counterparts and are particularly suitable to form a double emulsion. *N*-Isopropylacrylamide microgels (Kim *et al.* 2007) and acrylate capsules (Utada *et al.* 2005) have been fabricated with these devices.

A class of materials that has not been explored at all for the generation of monodispersed particles and capsules in microfluidic devices is preceramic polymers. Preceramic polymers are organic–inorganic polymers whose backbone usually contains Si atoms; they are transformed into a ceramic material through the elimination of organic moieties (by breaking of C–H bonds, and release of H₂ and CH₄ and other volatile compounds), either by heat (pyrolysis) or by some non-thermal process (e.g. ion irradiation). Upon heating, they convert into SiO₂, SiOC, SiC, SiCN, Si(X)CN or Si(X)O (with X = B, Al, Ti, Zr) ceramics, depending on their composition in the polymeric state and the processing conditions (e.g. inert or oxidizing atmosphere, maximum heating temperature (Colombo *et al.* 2009)). One of the main characteristics of preceramic precursors is that they are polymeric in nature at the temperature at which they are shaped into components. Therefore, they can be subjected to a large variety of different forming methods, some of them unique or at least much more easily exploitable for polymers than ceramic powders or pastes. These include casting (Melcher *et al.* 2003), infiltration (Satoa *et al.* 1999), pressing (Galusek *et al.* 2007), injection moulding (Walter *et al.* 1996), extrusion (Eom & Kim 2007; Eom *et al.* 2008), machining (Rocha *et al.* 2005), fibre drawing (Okamura *et al.* 2006), blowing/foaming (Colombo 2008), ink jetting (Mott & Evans 2001), rapid prototyping (Friedel *et al.* 2005), electrohydrodynamic spraying/spinning (Nangrejo *et al.* 2009), aerosol spraying (Bahloul-Hourlier *et al.* 2001), self-assembly (Malenfant *et al.* 2007) and micro-component processing such as UV/X-ray lithography, nano/micro-casting, replication, micro-extrusion and embossing/forging (Schulz 2009).

Furthermore, this approach has important technological advantages over the use of other molecular precursors, such as sol–gel techniques, as preceramic polymers do not need long processing times for gelation and drying, do not have any drying problems that hinder the possibility of fabricating bulk components, do not require flammable solvents, can be processed in the molten state, their solutions are stable in time and, at least for inexpensive, commercially available

polysiloxanes, they do not require any specialized handling procedures (Colombo *et al.* 2009). Finally, components fabricated from these precursors can be used in the polymeric state, i.e. without undergoing ceramization.

Electrohydrodynamic techniques have been used to generate nano- to microscale particles and capsules from preceramic polymers. Nangrejo *et al.* (2008) used methylsilsesquioxane to generate porous particles via electrospraying. These particles were nearly spherical with a diameter of 3 μm and have interconnected porosity with diameters close to 1.3 μm . Ahmad *et al.* (2009) also reported the formation of ceramic bubbles from preceramic polymers via electrospraying.

Surprisingly, there have been no reports concerning the processing of preceramic materials using microfluidic devices. Here, we present for the first time a robust microfluidic technique to generate monodispersed ceramic particles and capsules from preceramic polymers using microcapillary devices. The technique is based on the formation of monodispersed single emulsion and double emulsion drops using a preceramic polymer. These drops are then cross-linked and pyrolysed to form ceramic particles and capsules. This versatile technique can be extended to other preceramic polymers and the device geometry can be modified to fabricate monodispersed particles and capsules with diameters as small as 10 μm .

2. EXPERIMENTAL SET-UP

2.1. Emulsion solutions

Several solutions were used to fabricate the single and double emulsion drops described in this work. All of them share a similar preceramic solution and continuous fluid. The preceramic solution was composed of 60 wt% poly(methylsilsesquioxane) (MK powder, Wacker International), 1 wt% Zr-acetylacetonate (cross-linker, Sigma, St Louis, MO), 2 wt% (decamethylcyclopentasiloxane with trimethylated silica (749 fluid, Dow Corning, Midland, MI)) surfactant in 1 cSt octamethyltrisiloxane oil (Clearco Products, Bensalem, PA). The continuous fluid is a mixture of 58 wt% DI-H₂O, 40 wt% glycerol (ReagentPlus less than or equal to 99.0% (GC), Sigma) and 2 wt% poly(vinyl alcohol) (PVA) (87–89% hydrolysed, Sigma), which served as a surfactant. An emulsion of DI-H₂O in the preceramic solution was used in the fabrication of porous particles and capsules. A 1:2 ratio by volume of DI-H₂O in preceramic solution was emulsified using a homogenizer (VDI-12, VWR West Chester, PA) rotating at 13 500 r.p.m. for 5 min. Finally, a 0.5 wt% Zr-acetylacetonate in DI-H₂O was used as the inner fluid in the fabrication of solid and porous capsules. Table 1 summarizes the four fluids used in this work.

2.2. Device preparation

The microcapillary devices' geometry was based on the work by Utada *et al.* (2005) and a full description of the device fabrication process can be found elsewhere.

Table 1. Compositions of the four fluids used to generate ceramic solid and porous particles and capsules from preceramic polymers.

fluid	composition
inner fluid	1 wt% Zr-acetylacetonate (cross-linker) in DI-H ₂ O
outer fluid	40 wt% glycerol and 2 wt% poly(vinyl alcohol) (PVA) in DI-H ₂ O
preceramic solution	1 wt% Zr-acetylacetonate, 0.6 g ml ⁻¹ poly(methylsilsesquioxane) (MK powder), 2 wt% 749 fluid (surfactant) in 1 cSt polydimethylsiloxane (PDMS) oil
preceramic emulsion	emulsion of DI-H ₂ O in the preceramic solution (1 : 2 volume ratio)

Briefly, a pipette puller (model P-97, Sutter Instruments, Novato, CA) was used to heat and pull a 15.24 cm long cylindrical glass capillary (World Precision Instruments, Sarasota, FL) with an outer diameter of 1.0 mm and inner diameter of 0.580 mm. The glass capillary breaks under tension into two equal-sized, tapered capillaries. The tapered glass capillaries were then cleaved to the desired final diameters using a forge station (Micro Forge MF 830, Narishige, Japan). Typical diameters of the input (d_{input}) and exit (d_{exit}) capillaries ranged from 20 to 300 μm . Tips were treated to be hydrophobic or hydrophilic by surface modification with octadecyltrichlorosilane (Gelest, Inc., Morrisville, PA) or a solution of ethanol (reagent grade, Sigma), acetic acid (99.7 + % A.C.S. reagent, Sigma), DI-H₂O and 2-[methoxy(polyethylenoxy)propyl] trimethoxysilane (90%, Gelest, Inc.), respectively. The round capillaries were then inserted and aligned in a square capillary. Choosing the outer diameter of the round capillaries to be the same as the width of the square capillary facilitates alignment. Three 20G luer-stubs (Intramedic Luer Stub Adapters, Beckton Dickinson, Sparks, MD) served as input connectors for the fluids. A schematic of the microcapillary device and the region of the device where the two tapered capillaries meet is shown in figure 1*a,b,e*, respectively.

2.3. Single and double emulsion fabrication

Fluids for emulsion fabrication were loaded into glass syringes (Hamilton Gastight, Hamilton Co., Reno, NV) fitted with 20G luer-stubs. The syringes were connected to the luer-stub inputs using polyethylene PE-5 tubing with an outer diameter of 1.32 mm and inner diameter of 0.86 mm (Scientific Commodities, Lake Havasa City, AZ). Syringe pumps (PHD 2000, Harvard Apparatus, Holliston, MA) were used to control the fluid flow rates. Droplet production was visualized in an inverted microscope (Axio Observer, Zeiss America) equipped with a fast-camera (Phantom V9, Vision Research, Wayne, NJ) capable of up to 55 000 frames s⁻¹. Emulsions were generated by individually adjusting the fluid flow rates. Optical images of the collected drops and cross-linked capsules were captured in the inverted microscope fitted with a QICAM digital camera (Qimaging, Surrey, BC, Canada).

2.4. Drop collection, cross-linking and pyrolysis

All drops were collected in a glass vial filled with either pure DI-H₂O or a mixture of DI-H₂O and glycerol designed to match the osmotic pressure in the inner drops. In many cases, the outer fluid was replaced several times to remove the excess of glycerol and PVA from the outer fluid during the collection process. Vials containing the emulsion drops were completely filled with 0.5 wt% Zr-acetylacetonate in DI-H₂O solution and placed in an oven preset to a temperature of 80°C for 18 h to accelerate the cross-linking of the preceramic solution. Cross-linked particles and capsules were washed with a 1 : 1 mixture of isopropyl alcohol and water to remove any excess PDMS oil. The samples were then freeze-dried to remove the water while preserving their structure. Pyrolysis was performed in an inert atmosphere (N₂, 99.99%) by heating at a rate 5°C min⁻¹ to a temperature of 1000°C, held for 1 h and cooled to room temperature at a rate of 5°C min⁻¹.

2.5. Drop and particle characterization

Optical images of the single and double emulsion drops were analysed with the freely available image analysis program, ImageJ (W. S. Rasband, US National Institutes of Health, Bethesda, MD). Characterization of the cross-linked and pyrolysed particles was performed in a scanning electron microscope (SEM; FEI Philips XL-40; Angstrom Scientific Inc., Ramsey, NJ). XRD analysis was carried out with a Bruker D8 Focus X-Ray system (Bruker AXS Inc., Madison, WI). FT-IR was carried out in a Spectrum System 2000 (Perkin-Elmer, Waltham, MA).

3. RESULTS AND DISCUSSION

The particle and capsule fabrication technique presented here rests on the generation of monodispersed single and double emulsion drops using microcapillary devices. These devices were operated in either single or double emulsion mode depending on the desired particles. Solid and porous particles were obtained from single emulsions, while the solid and porous capsules were obtained from double emulsion drops (see figure 1). Key to this fabrication is the transformation of the drops into solid objects via the cross-linking and pyrolysis of the preceramic solution. In particular, cross-linking is a crucial step for enabling the manufacturing of samples with controlled geometry. In fact, if the preceramic polymer is not sufficiently cross-linked, during subsequent pyrolysis it would be subjected to softening and flow, resulting in highly deformed or fused particles. Moreover, gases are generated during the polymer-to-ceramic conversion occurring during pyrolysis, which could lead to damaged samples, so the heat treatment schedule has to be conducted in a well-controlled fashion. The selected processing conditions enabled the production of defect-free, individually separated ceramic particles and capsules whose morphology followed closely that of the as-prepared, polymeric components. Pyrolysis resulted only in a linear shrinkage of approximately 25 per cent,

Figure 1. Schematic illustrations of (a) the overall microcapillary microfluidic device and (b) microcapillary device used for generating single emulsion drops, (c) solid particles and (d) porous particles produced from single emulsions; (e) microcapillary device used for generating double emulsions, (f) solid capsules and (g) porous capsules produced from double emulsions.

relative to un-pyrolysed samples, which is typical for this type of preceramic precursor (Colombo *et al.* 2009). A full description of the fabrication of each of the particles and capsules follows.

3.1. Monodisperse single emulsions

3.1.1. Solid particles. Solid particles were fabricated by operating the microcapillary device in single emulsion mode, as shown in figure 1b, to generate monodispersed drops of the preceramic solution in the continuous

solution. The continuous solution was loaded into the microcapillary device through the outer and middle fluid inputs, where it flowed in the space between the inner and exit capillaries in opposite directions, as shown in figure 1b. The preceramic solution was loaded into the device through the inner fluid input and the input round capillary. Outer and inner fluids met near the entrance of the exit capillary and, after adjusting the flow rates, drops began to drip from the inner tip and move through the exit capillary where they were then collected in a cross-linker/DI-H₂O

Figure 2. Optical images of (a) the formation of single emulsion drops near the entrance of the exit capillary (scale bar, 100 μm). (b) Optical image of a group of cross-linked preceramic solid particles (scale bar, 50 μm). (c) SEM micrograph of an oxycarbide solid glass particle (scale bar, 5 μm).

solution. The formation of single emulsion drops can be seen in figure 2a. Drops had a diameter of 100 μm and a coefficient of variation (CV) in diameter less than 3 per cent. Flow rates were: outer fluid ($Q_{\text{outer}} = 2000 \mu\text{l h}^{-1}$) and inner fluid ($Q_{\text{inner}} = 1000 \mu\text{l h}^{-1}$) for the sample in figure 2a.

Drop break-up in this device is controlled by the interplay between viscous forces and interfacial tension between the liquids. Two mechanisms can be observed depending on the fluid flow rate ratios, namely dripping and jetting. In dripping, the inner drop breaks from the end of the capillary into the entrance of the exit capillary due to the Rayleigh–Plateau instability (Plateau 1849; Rayleigh 1879). Dripping produces highly monodispersed drops. In the jetting regime, the inner fluid forms a jet that extends into the exit capillary. A drop forms at the tip of the jet and it breaks at

random intervals forming polydispersed drops. A jet forms when the velocity or viscosity of the outer fluid is significantly larger than that of the inner fluid, so that viscous stresses at the interface dominate over the interfacial tension, as demonstrated by Utada *et al.* (2005). The physics can be captured in the capillary number (Ca), which relates the ratio of the viscous stresses and interfacial tension,

$$Ca = \frac{\eta_{\text{out}} v}{\gamma}, \quad (3.1)$$

where η_{out} is the viscosity of the outer fluid, v is the velocity of the outer fluid and γ is the interfacial tension between the outer and inner fluid. The equation governs the transition between the dripping and jetting regimes which occurs at $Ca \approx 1$ (Utada *et al.* 2005). In all of our experiments, the fluid conditions were optimized to ensure operation in the dripping regime to obtain monodispersed drops.

The monodispersed single emulsion drops were then cross-linked in solution. An optical image of a group of cross-linked preceramic particles is shown in figure 2b. The particles are spherical and show no damage on the surface. These were dried and pyrolysed to form oxycarbide glass particles. An SEM micrograph showing a pyrolysed particle can be seen in figure 2c. The particles have maintained their spherical shape and there is minimal indication of damage at the surface. After pyrolysis, the particles can be redispersed in water or used as they are for biological applications such as cell respiration experiments and cell break-up for DNA extraction.

3.1.2. Porous particles. Inert porous particles can be used in many bioapplications, including trapping of biomolecules (Liu & Chen 1999; Cunin *et al.* 2002) and scaffolds for cell growth (Rezwan *et al.* 2006). We were interested in modifying our single emulsion technique to generate monodispersed porous particles. Our aim was to generate particles and capsules with relatively large interconnected pores with diameters in the range of 1–10 μm for applications as substrates for enzymatic reactions. The preceramic solution used for the solid particles was replaced with DI- H_2O in the preceramic solution emulsion. The drops of water in the emulsion act as pore generators after cross-linking and freeze-drying of the samples. Image analysis of the emulsions shows that the water drops have a wide diameter distribution ranging from 0.5 to 7 μm and a CV in diameter of 55 per cent. Monodispersed drops containing the emulsion were generated using the same devices and procedures described before for solid particle fabrication. An optical image of the drop generation process can be seen in figure 3a. For this sample, the $Q_{\text{inner}} = 650 \mu\text{l h}^{-1}$, Q_{middle} and $Q_{\text{outer}} = 1000 \mu\text{l h}^{-1}$ and the average diameter was 72 μm . The water droplets appear as dark spots within the circular area delineating the monodispersed drops. An emulsion with small drops relative to the capillary diameters was necessary to avoid an abrupt disruption of the fluid flow during the drop generation. Particles were cross-linked using the same procedure previously described for the

Figure 3. Optical images of (a) the generation of single emulsion drops containing a water/preceramic solution emulsion (scale bar, 100 μm) and (b) a group of cross-linked preceramic particles with water drops through their volume (scale bar, 50 μm).

solid particles. An optical image showing an array of monodispersed cross-linked drops can be seen in figure 3b. Each of the speckles within the drops is a smaller water droplet. Note the uniform diameter of the cross-linked drops with an average diameter 82 μm and a CV less than 3 per cent. The drops were stable during the cross-linking process. There was no evidence of coalescence of water droplets either within the drops or between the drops themselves. However, we observed an increase in water droplet size over time, most probably due to Ostwald ripening and/or osmotically driven flow of water molecules to the water droplet from the continuous phase. Glycerol and/or salt was therefore added to both the continuous phase and water droplets in the range 0.5–2 wt% to match the osmotic pressures, and minimize the changes in the size of the water droplets. Despite these efforts, we always observed an increase in the drop diameter over time. PDMS oil is well known for its relatively high water content and for the facile transport of water molecules (Randall & Doyle 2005). However, it is possible to harness this behaviour to increase the pore size of particles or capsules. For example, the overall size of the drops can be increased by increasing the solute concentration in the water droplets, while keeping the solute concentration low in the continuous phase. The osmotic difference drives water into the water droplets inside the drop, increasing their overall size until the osmotic pressure is matched.

The cross-linked porous particles were harvested from solution, freeze-dried and pyrolysed following similar procedures as described for the solid particles. These particles are over 100 μm in diameter and contain pores

Figure 4. SEM micrographs of (a) a group of pyrolysed oxycarbide glass porous particles (scale bar, 100 μm), (b) a single porous oxycarbide glass particle (scale bar, 20 μm) and (c) the internal porous structure of a broken porous oxycarbide glass particle (scale bar, 20 μm).

in the surface with diameters ranging from 1 to 10 μm , as can be seen on the particle surface shown in figure 4a,b. The pores do not have a perfect circular shape and smaller pores appear more circular than the larger ones. The surface porosity is interconnected with the internal porosity, as shown in the broken particle in figure 4c. Note the large amount of porosity in the interior of the particle; since this is accessible to the exterior it offers a large amount of surface area for the binding of enzymes or proteins. Note that, while we fabricated larger porous particles as a proof of concept, smaller particles can be easily generated down to a diameter of 10 μm . For example, to make 10 μm particles requires a microcapillary device with

Figure 5. Optical images of (a) the formation of double emulsion drops near the entrance of the exit capillary and (b–d) cross-linked preceramic solid capsules with different diameters and shell thicknesses (scale bars, 100 μm).

an input capillary diameter of 10 μm and an exit capillary diameter close to 20 μm . Besides these device changes, the flow rates would need to be adjusted

independently to obtain the desired drop size. Porous-wall glass microspheres have found application in drug delivery and controlled release of biological molecules (Li *et al.* 2009). This can be achieved using microcapillary devices with inner and exit capillary diameters comparable to the drop diameter of interest.

3.1.3. Solid capsules. Three different fluids are needed to generate monodispersed double emulsion drops. In the microcapillary devices, the inner fluid (Zr-acetyl-acetate/water) is pumped through the input round capillary, while the middle fluid (preceramic solution) is pumped in the same direction through the outer round/square capillary region. The outer fluid (continuous solution) is also pumped through the round and square capillary region, but in the opposite direction. As the three fluids merge near the entrance of the exit capillary, the outer fluid hydrodynamically focuses the inner and middle fluid and double emulsion drops are formed in a single step. Typical tapered diameters for the input and exit round capillaries range from 20 to 180 μm ; however, smaller or larger sizes can also be fabricated, which permit the drop size to be adjusted further. For a given device geometry, we can further adjust the inner and outer drop diameters and the number of internal drops, by carefully tuning the fluid flow rates and composition. Fabrication rates ranging from 200 to 5000 drops s^{-1} can be achieved in these devices depending on the fluid flow rates and device geometry.

The formation of the monodispersed double emulsion drops with this composition is shown in figure 5a. Flow rates were: inner ($Q_{\text{inner}} = 1000 \mu\text{l h}^{-1}$), middle ($Q_{\text{middle}} = 1000 \mu\text{l h}^{-1}$) and outer ($Q_{\text{outer}} = 5000 \mu\text{l h}^{-1}$). Average inner and outer drop sizes initially were 75 and 100 μm , respectively, as determined from the optical images. The viscosity of the outer fluid (η_{outer}) is estimated to be 3.7 mPa s, while the middle fluid (η_{middle}) is 0.960 mPa s, giving a ratio ($\eta_{\text{outer}}/\eta_{\text{inner}}$) of 3.87. Double emulsions generated with this composition were stable through the cross-linking process. There was no evidence of inner drop break-up from the surrounding oil drop or the coalescence of the outer drops.

Double emulsions were collected in DI- H_2O , and any excess glycerol in the outer fluid was removed via repeated washing with a cross-linker/DI- H_2O /PVA solution to ensure that enough surfactant was left in the solution. The cross-linked capsules appear to change little with time and they maintained their monodispersity. Optical images of the cross-linked capsules with different diameters and shell thicknesses can be seen in figure 5b–d. The capsules in figure 5b have an average outer diameter = 37.8 μm and inner diameter = 21 μm with a CV less than 3 per cent. Capsules in figure 5c have an average outer diameter = 98.1 μm and inner diameter = 77.1 μm with a CV less than 4 per cent. Capsules in figure 5d have an average outer diameter = 164.1 μm and inner diameter = 102.5 μm with a CV less than 3 per cent. The small CV for all samples indicates that these capsules are highly monodispersed, as can be seen by the narrow inner and

Figure 6. (a) Inner and outer diameter distribution for pre-ceramic solid capsules with an average outer diameter of $37\text{ }\mu\text{m}$ and inner diameter of $21\text{ }\mu\text{m}$. (b) Inner and outer drop diameter as a function of $Q_{\text{outer}}/(Q_{\text{inner}} + Q_{\text{middle}})$ for drops generated using a device with input and exit capillary diameters of 40 and $80\text{ }\mu\text{m}$, respectively (filled diamond, inner drop; filled circle, outer drop).

outer drop diameter distributions (for the sample in figure 5b) reported in figure 6a.

To illustrate the flexibility of our technique in tailoring capsule size, the inner and outer drop diameters as a function of $Q_{\text{outer}}/(Q_{\text{inner}} + Q_{\text{middle}})$ are shown in figure 6b. These data were obtained using a device with inner and exit capillary diameters of 40 and $80\text{ }\mu\text{m}$, respectively. Additionally, $(Q_{\text{inner}} + Q_{\text{middle}})$ was kept constant to $2000\text{ }\mu\text{l h}^{-1}$, while Q_{outer} was changed from $2000\text{ }\mu\text{l h}^{-1}$ to $16\,000\text{ }\mu\text{l h}^{-1}$. Over this range the outer drop diameter decreased from 128 to $53\text{ }\mu\text{m}$ while the inner drop decreased from 101 to $41\text{ }\mu\text{m}$. Also, in this range the shell thickness decreased from 27 to $12\text{ }\mu\text{m}$. The shell thickness can be further tailored by independently adjusting the flow rates, in particular Q_{inner} . For example, increasing Q_{inner} while keeping Q_{outer} and Q_{middle} constant will result in a thinner shell, while a thicker shell is obtained at lower Q_{inner} .

Cross-linked capsules have an off-centre cavity (see figure 5). This is due to the difference in density between the inner and middle fluids. The aqueous solution in the inner drop has a density of 1 g cm^{-3} while the outer drop, which is mostly 1 cSt PDMS oil, has a measured density of 0.94 g cm^{-1} . Therefore, immediately after the double emulsion drops are generated, the inner droplet starts to sediment until it touches the outer drop/continuous phase interface. We estimate that the sedimentation occurs in a matter of seconds after drop generation. Different unsuccessful strategies were explored to centre the inner drop before cross-linking, including placing the emulsion in a tumbling wheel to keep the drops in constant motion and increasing the middle fluid density and viscosity. An unexplored potential solution is to incorporate a UV-cross-linkable polymer in the preceramic solution to slightly cross-link the middle fluid immediately after the drops are generated, when the inner and outer drops are usually centred with respect to each other.

Capsules have a high content of PDMS oil in the shell after cross-linking. Therefore, excess PDMS oil was removed by repeatedly washing the double emulsions in a $1:1$ volumetric ratio of isopropanol (IPA) and $\text{DI-H}_2\text{O}$ followed by repeated washing with $\text{DI-H}_2\text{O}$. Diluting the IPA in water was necessary to avoid a significant softening of the capsule shells, which makes them sticky in solution. Harvesting the capsules from solution by drying under ambient conditions resulted in pronounced deformation, owing to the capillary pressure inside and outside the capsules. An effective strategy to avoid deformation was to freeze-dry the capsules. Freeze-dried samples were prepared by removing most of the fluid, followed by rapidly freezing the sample and the subsequent sublimation of the frozen water in a vacuum. Freeze-dried capsules maintain their spherical shape and the capsule structure is intact.

Capsules were pyrolysed under an inert atmosphere to form an oxycarbide glass. An SEM micrograph of the pyrolysed capsules is shown in figure 7a. These capsules have an average diameter of $25\text{ }\mu\text{m}$ and all have a non-uniform shell thickness. A portion of the capsule has a slight deformation in a small area located in the thinnest part of the shell. This thin region of the capsule becomes its weakest point. An individual broken SiOC glass capsule can be seen in figure 7b. We estimate the thinnest area of the shell to be $1\text{--}3\text{ }\mu\text{m}$ in thickness, from optical and SEM images. Higher magnification SEM images (not shown) indicated that the surfaces of the capsules have rough undulations at the submicron scale size.

Capsules with solid shells can find widespread use as additives in the automotive, heavy truck, aerospace, electrical, electronics, appliance and durable goods industries, and in construction products such as polymer/wood composites and siding. They are also used in syntactic foams, associated with a polymeric, metallic or ceramic matrix, for applications such as stress absorption, acoustic insulation, lightweight parts, buoyancy modules, radar-transparent components, blast mitigation or thermal management (Shutov 1986; Cochran 1998).

Figure 7. SEM micrographs of (a) a group of pyrolysed oxy-carbide glass capsules (scale bar, 20 μm) and (b) a broken capsule showing the inner cavity (scale bar, 5 μm).

3.1.4. Porous capsules. Double emulsion drops were also generated with the water/preceramic emulsion. An optical image of the double emulsion fabrication process can be seen in figure 8a. For this sample, the $Q_{\text{inner}} = 1000 \mu\text{l h}^{-1}$, $Q_{\text{middle}} = 600 \mu\text{l h}^{-1}$ and $Q_{\text{outer}} = 4000 \mu\text{l h}^{-1}$ and the average diameter was 92 μm . The inner and outer drop diameters can be tailored by adjusting the fluid flow rates and device geometry. The internal composition of these drops is different from those previously discussed for the capsules or porous particles. Instead of having a single inner drop, as in the case of the solid capsules, these have a large water drop in the centre surrounded by smaller ones from the water/preceramic emulsion. A delicate balance between the larger drop, smaller droplets and the continuous phase must be preserved to avoid significant drop size changes. The solute concentration in the continuous phase and water droplets must be equal to avoid significant size changes due to an osmotic pressure gradient. Therefore, NaCl was added to the inner aqueous solutions to match the osmotic pressure to the continuous phase. These modifications to the drop composition do not have a large effect on the size changes that occur in the water/preceramic emulsion due to Ostwald ripening. For example, it is possible to reduce the size of the central drop by having a high solute concentration in the continuous phase and in the water droplets in the water/preceramic emulsion. The inner water drop shrinks to increase the solute concentration while the

Figure 8. Optical images of (a) the generation of double emulsion drops containing a water/preceramic emulsion in the middle fluid (scale bar, 100 μm) and (b) a group of cross-linked capsules with a large water drop in the centre surrounded by smaller water droplets (scale bar, 50 μm).

smaller water drops increase in size to equilibrate the osmotic pressure. Therefore, the final size of the inner drop can be further tailored depending on the water composition both within the drops and in the continuous phase.

Cross-linked capsules with water droplets can be seen in figure 8b. The average inner and outer diameters of the capsules were 58 and 95 μm , respectively, with a CV of less than 5 per cent for the outer diameter. These capsules maintained their shape during the PDMS oil cleaning process. However, they did not maintain a spherical shape after freeze-drying and pyrolysis; this can be seen in the SEM micrograph in figure 9a, which shows a group of SiOC glass porous capsules. The surface of the shells is highly porous, with pore diameters in the range of 1–10 μm . The porosity in the shell and the lack of an internal structure makes these capsules mechanically fragile, and results in deformed shells (Rachik *et al.* 2006). The shell has a thickness of 5–10 μm , as can be seen in the broken capsule in figure 9b. It might be possible to use these capsules as bio-reservoirs by filling them with biomaterials after fabrication.

Finally, it should be stressed that by varying the processing conditions it is possible to modify the shell thickness of solid and porous capsules; this, in turn, results in changes in their mechanical and release behaviour (Rachik *et al.* 2006), as well as in the volume fraction of ‘cargo’ that they can accommodate in their central cavity.

Figure 9. SEM micrographs of (a) a group of pyrolysed oxycarbide glass porous capsules (scale bar, 100 μm) and (b) a broken pyrolysed oxycarbide glass capsule (scale bar, 50 μm).

4. CERAMIZATION OF PARTICLES AND CAPSULES

In this work, we processed the particles and capsules under an inert atmosphere, as we intended to produce SiOC ceramic samples and not simply silica-based components (as we would have produced if heating in air). In SiOC materials, in fact, carbon is substituted for oxygen within the SiO matrix, greatly strengthening the molecular structure of the resulting glass network. Silicon is thus simultaneously bonded to carbon and oxygen and, depending on the composition of the precursor, the carbon content can be as high as 70 mol% (Scheffler *et al.* 2000). Because of their structure, SiOC glasses have tailorable physical properties that strongly depend on the microstructure (presence of phase separation and bonding state of carbon) and composition (carbon content). They exhibit remarkable mechanical properties, including high elastic modulus, bending strength and hardness; resistance to oxidation at high temperature, devitrification and creep; and chemical durability superior to conventional silicate glasses in aggressive environments (Eguchi & Zank 1998; Pantano *et al.* 1999). In particular, they have been shown to possess a variable propensity to contact activate coagulation of whole human blood plasma, depending on the carbon/oxygen ratio at their surface. Therefore, simply by changing the preceramic precursor it is possible to vary the plasma activation properties of the resulting SiOC ceramic from activating (e.g. similar to silica glass) to non-activating (e.g. similar to silanized glass (Zhuo *et al.* 2005)). Moreover, through the addition of nano-sized

Figure 10. (a) Transmittance as a function of wavelength for the preceramic capsules cross-linked in solution and the oxycarbide glass samples after pyrolysis at 1000°C in nitrogen. (b) X-ray diffraction profile as a function of scanning angle for the oxycarbide glass capsules after pyrolysis at 1000°C in nitrogen.

fillers to a siloxane precursor it is possible to obtain ceramic components based on wollastonite (CaSiO_3 (Bernardo *et al.* 2009)), which possesses excellent bioactivity (Xue *et al.* 2005).

After pyrolysis, the samples comprised an amorphous silicon oxycarbide ceramic. FT-IR investigations (figure 10a) showed the complete removal of the organic moieties present in the preceramic polymeric precursor, after heating at 1000°C, with the retention of Si-C bonds in the material. Specifically, peaks relative to the Si-CH₃ (at approx. 1410, 1275, 1127, 770 cm^{-1}) and C-H bonds (approx. 2980 cm^{-1}), present in the as-produced preceramic samples, disappeared, leaving only those peaks related to Si-O (1090, with the shoulder at approx. 1200 cm^{-1} , 800 and 460 cm^{-1}) and Si-C bonds (800 cm^{-1}) in the ceramized component (Bellamy 1975). XRD analysis (figure 10b) confirmed the lack of crystalline phases at this processing temperature, as only the amorphous hump located at around 22°, attributable to an amorphous silica-based phase, was visible. The data reported here were collected on porous capsules, but similar results were obtained for solid and porous particles and solid capsules, naturally,

Figure 11. Pore size distribution for porous ceramic (a) particles and (b) capsules, after pyrolysis at 1000°C in nitrogen.

as they were produced using the same preceramic precursor and the added surfactants completely decomposed during pyrolysis. These data are in good agreement with what has been reported in the literature concerning the pyrolysis product of this specific silicone resin (Harshe *et al.* 2004).

Figure 11 shows the distribution of the pore size for porous ceramic particles and capsules, as obtained by image analysis of SEM micrographs of several samples. By 'pore', we mean the dimension of the empty cells formed in the solid ceramic by the evaporation of the water droplets present within the liquid preceramic precursor and constituting the emulsion. It can be observed that, although the average pore size is rather similar for both types of samples (5.8 μm for particles and 4.1 μm for capsules), the size distribution is smaller for the latter (standard deviation was 2.4 μm for particles and 1.4 μm for capsules), indicating that, with increasing thickness of the layer containing the preceramic/water emulsion, it is more difficult to control the uniformity of the size of the water droplets. It should, however, be noted that it is quite difficult to comment on the permeability of these structures based on simple considerations of the average pore size, as the porosity of the samples possesses a foam-like morphology, and therefore the permeability is controlled by the dimension of the cell windows and the presence of cell walls, which cannot be easily quantified by optical methods (Maire *et al.* 2007).

Controlling the drop size in the preceramic emulsion is critical for tuning the pore size distribution in the particles and capsules. We emulsified the water in the preceramic solution using a homogenizer. This process always leads to a broad drop diameter distribution. We could narrow the distribution by fractionation but the process is cumbersome and tedious. The best way to control the drop distribution is to use the microcapillary devices to generate monodispersed drops. This will require the use of capillaries with diameters comparable to the desired drop diameter, in our case between 1 and 10 μm. Also, it is possible to change the chemistry in the preceramic solution to generate a microemulsion instead of an emulsion. Microemulsions have a narrow drop size distribution and the average drop size is between 20 and 500 nm, effectively reducing the pore size by one order of magnitude.

5. CONCLUSIONS

We have developed a robust microfluidic technique to generate monodispersed ceramic particles and capsules from a preceramic polymer. The technique harnesses the versatility of microcapillary devices to generate monodispersed single emulsion and double emulsion drops in a single step. Poly(methylsilsesquioxane) was used as the preceramic polymer leading to the formation of oxycarbide glass particles and capsules after pyrolysis. Four types of particles and capsules were generated with this technique, including solid particles, solid capsules, porous particles and porous capsules. Solid particles and solid capsules had diameters ranging from 30 to 180 μm, and both maintained their structure during all the processing steps. Porous particles and capsules were generated by substituting the preceramic mixture with a water/preceramic emulsion. Water drops within this emulsion served as pore generators in the particles and capsules after freeze-drying and pyrolysis. Porous particles, with diameters ranging from 55 to 110 μm, had an interconnected porosity that was open to the exterior with pore diameters in the range 1–10 μm. Porous capsules had a large cavity in the centre and similar pore sizes in the shell to the porous particles. Particle and capsule diameters can be easily reduced to less than 10 μm by changing the device geometry, fluid composition and flow rates. Pore sizes could also be reduced by using a microemulsion instead of an emulsion as the preceramic solution.

This work demonstrates that it is possible to use microfluidics to process preceramic polymers to generate monodispersed porous particles and capsules. There are hundreds of different preceramic polymers with different compositions, functionalities and solubility characteristics. One key aspect that enabled drop fabrication was the high solubility of the preceramic polymer in 1 cSt PDMS oil. This is convenient but not a requirement for other preceramic polymers, since it is possible to use organic solvents such as toluene or acetone to generate drops. Compared with electrohydrodynamic techniques, our method provides excellent control over the drop/capsule size and composition and it does not require conductive fluids for

operation. However, the range of drop and capsule sizes that can be fabricated is practically limited to more than 10 μm , while electrohydrodynamic methods can generate submicron drops and capsules albeit with a broader size distribution.

An immediate application of the porous oxycarbide particles is as scaffolds for the enzymatic detection of marine toxin such as okadaic acid in fish (Holland & Weber 2000; Marquette & Blum 2006). The solid particles could be used as grinding material for DNA extraction from cells (Shakoori *et al.* 1972). The possibility of expanding this work to other preceramic polymers, increased drop size range, varied drop morphologies and novel applications is great, and we are looking forward to pursuing these opportunities.

REFERENCES

- Ahmad, Z., Nangrejo, M., Edirisinghe, M. E., Stride, E., Colombo, P. & Zhang, H. B. 2009 Engineering a material for biomedical applications with electric field assisted processing. *Appl. Phys. A: Mater. Sci. Process.* **97**, 31–37. (doi:10.1007/s00339-009-5359-z)
- Akartuna, I., Tervoort, E., Studart, A. R. & Gauckler, L. J. 2009 General route for the assembly of functional inorganic capsules. *Langmuir* **25**, 12 419–12 424. (doi:10.1021/la901916q)
- Bahloul-Hourlier, D., Doucey, B., Laborde, E. & Goursat, P. 2001 Investigations on thermal reactivity of Si/C/N nanopowders produced by laser aerosol or gas interactions. *J. Mater. Chem.* **11**, 2028–2034. (doi:10.1039/b009162f)
- Bellamy, L. J. 1975 *Infra-red spectra of complex molecules v. 1*. London, UK: Chapman and Hall.
- Bernardo, E., Tomasella, E. & Colombo, P. 2009 Development of multiphase bioceramics from a filler-containing preceramic polymer. *Ceram. Int.* **35**, 1415–1421. (doi:10.1016/j.ceramint.2008.07.003)
- Caruso, F., Caruso, R. A. & Möhwald, H. 1998 Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating. *Science* **282**, 1111–1114. (doi:10.1126/science.282.5391.1111)
- Chen, J. *et al.* 2005 Gold nanocages: bioconjugation and their potential use as optical imaging contrast agents. *Nano Lett.* **5**, 473–477. (doi:10.1021/nl047950t)
- Cochran, J. K. 1998 Ceramic hollow spheres and their applications. *Curr. Opin. Solid State Mater. Sci.* **3**, 474–479. (doi:10.1016/S1359-0286(98)80010-7)
- Colombo, P. 2008 Engineering porosity in polymer-derived ceramics. *J. Eur. Ceram. Soc.* **28**, 1389–1395. (doi:10.1016/j.jeurceramsoc.2007.12.002)
- Colombo, P., Riedel, R., Soraru, G. D. & Kleebe, H. J. 2009 *Polymer derived ceramics: from nanostructure to applications*. Lancaster, PA: DETech Publications.
- Cunin, F., Schmedake, T. A., Link, J. R., Li, Y. Y., Koh, J., Bhatia, S. N. & Sailor, M. J. 2002 Biomolecular screening with encoded porous-silicon photonic crystals. *Nat. Mater.* **1**, 39–41. (doi:10.1038/nmat702)
- Dinsmore, A. D., Hsu, M. F., Nikolaidis, M. G., Marquez, M., Bausch, A. R. & Weitz, D. A. 2002 Colloidosomes: selectively permeable capsules composed of colloidal particles. *Science* **298**, 1006–1009. (doi:10.1126/science.1074868)
- Eguchi, K. & Zank, G. A. 1998 Silicon oxycarbide glasses derived from polymer precursors. *J. Sol-Gel Sci. Technol.* **13**, 945–949. (doi:10.1023/A:1008639727164)
- Eom, J. H. & Kim, Y. W. 2007 Fabrication of silicon oxycarbide foams from extruded blends of polysiloxane, low-density polyethylene (LDPE), and polymer microbead. *Metals Mater. Int.* **13**, 521–525. (doi:10.1007/BF03027913)
- Eom, J. H., Kim, Y. W., Song, I. H. & Kim, H. D. 2008 Processing and properties of polysiloxane-derived porous silicon carbide ceramics using hollow microspheres as templates. *J. Eur. Ceram. Soc.* **28**, 1029–1035. (doi:10.1016/j.jeurceramsoc.2007.09.009)
- Friedel, T., Travitzky, N., Niebling, F., Scheffler, M. & Greil, P. 2005 Fabrication of polymer derived ceramic parts by selective laser curing. *J. Eur. Ceram. Soc.* **25**, 193–197. (doi:10.1016/j.jeurceramsoc.2004.07.017)
- Galusek, D., Sedláček, J. & Riedel, R. 2007 Al_2O_3 -SiC composites prepared by warm pressing and sintering of an organosilicon polymer-coated alumina powder. *J. Eur. Ceram. Soc.* **27**, 2385–2392. (doi:10.1016/j.jeurceramsoc.2006.09.007)
- Harshe, R., Balan, C. & Riedel, R. 2004 Amorphous Si(Al)OC ceramic from polysiloxanes: bulk ceramic processing, crystallization behavior and applications. *J. Eur. Ceram. Soc.* **24**, 3471–3482. (doi:10.1016/j.jeurceramsoc.2003.10.016)
- Holland, H. L. & Weber, H. K. 2000 Enzymatic hydroxylation reactions. *Curr. Opin. Biotechnol.* **11**, 547–553. (doi:10.1016/S0958-1669(00)00142-7)
- Kim, J. W., Utada, A. S., Fernandez-Nieves, A., Hu, Z. & Weitz, D. A. 2007 Fabrication of monodisperse gel shells and functional microgels in microfluidic devices. *Angew. Chem. Int. Ed.* **46**, 1819–1822.
- Li, S., Nguyen, L., Xiong, H., Wang, M., Hu, T. C. C., She, J. X., Serkiz, S. M., Wicks, G. G. & Dynan, W. S. 2009 Porous-wall hollow glass microspheres as novel potential nanocarriers for biomedical applications. *Nanomed.: Nanotechnol. Biol. Med.* **6**, 127–136. (doi:10.1016/j.nano.2009.06.004)
- Liu, D. M. & Chen, I. W. 1999 Encapsulation of protein molecules in transparent porous silica matrices via an aqueous colloidal sol-gel process. *Acta Mater.* **47**, 4535–4544. (doi:10.1016/S1359-6454(99)00335-3)
- Lou, X. W., Wang, Y., Yuan, C., Lee, J. Y. & Archer, L. A. 2006a Template-free synthesis of SnO_2 hollow nanostructures with high lithium storage capacity. *Adv. Mater.* **18**, 2325–2329. (doi:10.1002/adma.200600733)
- Lou, X. W., Yuan, C., Zhang, Q. & Archer, L. A. 2006b Platinum-functionalized octahedral silica nanocages: synthesis and characterization. *Angew. Chem. Int. Ed.* **118**, 3909–3913.
- Maire, E., Colombo, P., Adrien, J., Babout, L. & Biasetto, L. 2007 Characterisation of the morphology of porous ceramics by 3D image processing of X-ray tomography data. *J. Eur. Ceram. Soc.* **27**, 1973–1981. (doi:10.1016/j.jeurceramsoc.2006.05.097)
- Malenfant, P. L., Wan, J., Taylor, S. T. & Manoharan, M. 2007 Self-assembly of an organic-inorganic block copolymer for nano-ordered ceramics. *Nat. Nanotechnol.* **2**, 43–45. (doi:10.1038/nnano.2006.168)
- Marquette, C. A. & Blum, L. J. 2006 Applications of the luminol chemiluminescent reaction in analytical chemistry. *Anal. Bioanal. Chem.* **385**, 546–554. (doi:10.1007/s00216-006-0439-9)
- Martinez, C. J., Hockey, B., Montgomery, C. B. & Semancik, S. 2005 Porous tin oxide nanostructured microspheres for sensor applications. *Langmuir* **21**, 7937–7944. (doi:10.1021/la050118z)
- Melcher, R., Cromme, P., Scheffler, M. & Greil, P. 2003 Centrifugal casting of thin-walled ceramic tubes from preceramic polymers. *J. Am. Ceram. Soc.* **86**, 1211–1213. (doi:10.1111/j.1151-2916.2003.tb03451.x)
- Mott, M. & Evans, J. R. G. 2001 Solid freeforming of silicon carbide by inkjet printing using a polymeric precursor. *J. Am. Ceram. Soc.* **84**, 307–313.

- Nangrejo, M., Ahmad, Stride, E., Edirisinghe, M. & Colombo, P. 2008 Preparation of polymeric and ceramic porous capsules by a novel electrohydrodynamic process. *Pharmaceut. Dev. Technol.* **13**, 425–432. (doi:10.1080/10837450802247929)
- Nangrejo, M., Bernardo, E., Colombo, P., Farook, U., Ahmad, Z., Stride, E. & Edirisinghe, M. 2009 Electrohydrodynamic forming of porous ceramic capsules from a preceramic polymer. *Mater. Lett.* **63**, 483–485. (doi:10.1016/j.matlet.2008.11.015)
- Nie, Z., Xu, S., Seo, M., Lewis, P. C. & Kumacheva, E. 2005 Polymer particles with various shapes and morphologies produced in continuous microfluidic reactors. *J. Am. Chem. Soc.* **127**, 8058–8063. (doi:10.1021/ja042494w)
- Nie, Z., Li, W., Seo, M., Xu, S. & Kumacheva, E. 2006 Janus and ternary particles generated by microfluidic synthesis: design, synthesis, and self-assembly. *J. Am. Chem. Soc.* **128**, 9408–9412. (doi:10.1021/ja060882n)
- Okamura, K., Shimoo, T., Suzuya, K. & Suzuki, K. 2006 SiC-based ceramic fibers prepared via organic-to-inorganic conversion process—a review. *J. Ceram. Soc. Japan* **114**, 445–454. (doi:10.2109/jcersj.114.445)
- Okushima, S., Nisisako, T., Torii, T. & Higuchi, T. 2004 Controlled production of monodisperse double emulsions by two-step droplet breakup in microfluidic devices. *Langmuir* **20**, 9905–9908. (doi:10.1021/la0480336)
- Pantano, C. G., Singh, A. K. & Zhang, H. 1999 Silicon oxycarbide glasses. *J. Sol-Gel Sci. Technol.* **14**, 7–25. (doi:10.1023/A:1008765829012)
- Plateau, J. 1849 Quatrieme note sur de nouvelles applications curieuses de la persistance des impressions de la retine. *Bull. Acad. R. Soc. BA Belg.* **16**, 254–260.
- Rachik, M., Barthes-Biesel, D., Carin, M. & Edwards-Levy, F. 2006 Identification of the elastic properties of an artificial capsule membrane with the compression test: effect of thickness. *J. Colloid Interface Sci.* **301**, 217–226. (doi:10.1016/j.jcis.2006.04.062)
- Randall, G. C. & Doyle, P. S. 2005 Permeation-driven flow in poly (dimethylsiloxane) microfluidic devices. *Proc. Natl Acad. Sci. USA* **102**, 10 813–10 818. (doi:10.1073/pnas.0503287102)
- Rayleigh, L. 1879 On the capillary phenomena of jets. *Proc. R. Soc. Lond.* **29**, 71–97. (doi:10.1098/rspl.1879.0015)
- Rezwan, K., Chen, Q. Z., Blaker, J. J. & Boccaccini, A. R. 2006 Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering. *Biomaterials* **27**, 3413–3431. (doi:10.1016/j.biomaterials.2006.01.039)
- Rocha, R. M., Greil, P., Bressiani, J. C. & Bressiani, A. H. A. 2005 Complex-shaped ceramic composites obtained by machining compact polymer-filler mixtures. *Mater. Res.* **8**, 191–196.
- Satoa, K., Tezuka, A., Funayama, O., Isoda, T., Terada, Y., Kato, S. & Iwata, M. 1999 Fabrication and pressure testing of a gas-turbine component manufactured by a preceramic-polymer-impregnation method. *Composite Sci. Technol.* **59**, 853–859.
- Scheffler, M., Gambaryan-Roisman, T., Takahashi, T., Kaschta, J., Muenstedt, H., Buhler, P. & Greil, P. 2000 Pyrolytic decomposition of preceramic organo polysiloxanes. *Ceram. Trans.* **115**, 239–250.
- Schulz, M. 2009 Polymer derived ceramics in MEMS/NEMS—a review on production processes and application. *Adv. Appl. Ceram.* **108**, 454–460. (doi:10.1179/174367609X422171)
- Shah, R. K., Kim, J. W. & Weitz, D. A. 2010 Monodisperse stimuli-responsive colloidosomes by self-assembly of microgels. *Langmuir* **26**, 1561–1565.
- Shakoori, A. R., Romen, W., Oelschläger, W., Schlatterer, B. & Siebert, G. 1972 A new technique for the isolation of nucleoli from animal cells. *Hoppe-Seyler's Z. Physiol. Chem.* **353**, 1735–1748.
- Shepherd, R. F., Conrad, J. C., Rhodes, S. K., Link, D. R., Marquez, M., Weitz, D. A. & Lewis, J. A. 2006 Microfluidic assembly of homogeneous and janus colloid-filled hydrogel granules. *Langmuir* **22**, 8618–8622. (doi:10.1021/la060759+)
- Shutov, F. A. 1986 Syntactic polymer foams. *Adv. Polym. Sci.* **73**, 63–123.
- Utada, A. S., Lorenceau, E., Link, D. R., Kaplan, P. D., Stone, H. A. & Weitz, D. A. 2005 Monodisperse double emulsions generated from a microcapillary device. *Science* **308**, 537–541. (doi:10.1126/science.1109164)
- Walter, S., Suttor, D., Erny, T., Hahn, B. & Greil, P. 1996 Injection moulding of polysiloxane/filler mixtures for oxycarbide ceramic composites. *J. Eur. Ceram. Soc.* **16**, 387–393. (doi:10.1016/0955-2219(95)00120-4)
- Xu, X. & Asher, S. A. 2004 Synthesis and utilization of monodisperse hollow polymeric particles in photonic crystals. *J. Am. Chem. Soc.* **126**, 7940–7945. (doi:10.1021/ja049453k)
- Xue, W., Liu, X., Zheng, X. B. & Ding, C. 2005 *In vivo* evaluation of plasma sprayed wollastonite coating. *Biomaterials* **26**, 3455–3460. (doi:10.1016/j.biomaterials.2004.09.027)
- Zhuo, R., Colombo, P., Pantano, C. G. & Vogler, E. A. 2005 Silicon oxycarbide glasses for blood-contact applications. *Acta Biomater.* **1**, 583–589. (doi:10.1016/j.actbio.2005.05.005)
- Zoldesi, C. I. & Imhof, A. 2005 Synthesis of monodisperse colloidal spheres, capsules, and microballoons by emulsion templating. *Adv. Mater. (FRG)* **17**, 924–928. (doi:10.1002/adma.200401183)