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Advanced reactor engineering with 3D printing for the continuous-flow synthesis of silver nanoparticles.

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1 Chemical reagents employed

All chemicals and solvents employed in this work were purchased from commercial suppliers and employed without further purification. The resin employed to fabricate the reactors is commercially available Formlabs Clear FLGPCL02. Acetonitrile, iso-propanol, sodium borohydride (98%) and silver nitrate were purchased from VWR ANALYTICAL. Polyvinylpyrrolidone (PVP) with an average weight of 10000 was purchased from Sigma-Aldrich.

2 Design and fabrication of mCOBR

Two flow reactors (tubular and mini Continuous oscillatory baffled reactor) devices have been fabricated by Vat polymerisation technique of Additive manufacturing. This demonstrates the usefulness of AM in fabricating intricate complex structures which are difficult to achieve in other manufacturing process. CAD models of the TR and mOBR devices, pictured in Figure S 1A, were designed on CREO parametric, converted to .STL and fabricated using Form 2, Formlabs Stereolithography platform. Off-the-shelf CLEAR FLGPCL02 obtained from formlabs were used in fabricating the reactors, Figure S 1B. With fine polishing and spraying with lacquer post-processing, a transparent device can be achieved. The TR and mCOBR devices are designed with volumes of 2.7ml and 2.5ml respectively at a layer setting of 100 micron, although a higher resolution of 25microns can be achieved on the platform. A cross-section of the fabricated 2.5mm diameter reactor was obtained and measured, Figure S 1C, having a minimal deviation of 0.13mm from the actual model. The measured RMS surface roughness at 100 microns print setting was 2.9 µm using a Zygo NewView[™] 8300 coherence scanning interferometer.



Figure S 1: AM fabricated/3D printed mini Continuous oscillatory baffled reactor device have fine polishing and spraying with Lacquer.



Figure S 2: Using Form 2 AM plaform, which provides a large build platform, multiple reactors can be fabricated simultaneously. The tubular and mCOBR is pictured just after fabrication with the support structure still in place.

3 Chemical stability of fabrication cured resin

The samples were soaked in either isopropanol (i-PrOH), ethanol (EtOH), water and acetonitrile (MeCN) at room temperature for 24 hours. Afterwards, the samples were filtered out from the solvent and dried at 50 °C under high vacuum overnight.

Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere with PerkinElmer TGA 4000. The samples were stabilized in the starting temperature of 30 °C for 5 minutes and then heated to 900 °C with the rate of 10 °C/min.

Infrared (IR) spectra were measured with Bruker Alpha-spectrometer using 24 scans with resolution of 4 cm⁻¹.

Differential scanning calorimetry was done with a TA Q200-instrument under nitrogen atmosphere. The samples were ground in a mortar into a fine powder prior to measurement. The thermal history of the samples was normalized by heating the samples first to 180 °C and cooling them to -50 °C. The samples were then heated from -50 °C to 180 °C. The curves from the second heating scans are reported. The heating and cooling rates were 10 °C/min in all cases.

The TGA-results display a slight change in the thermal decomposition behavior of the samples (Figure S3 A). All samples decompose in two steps (Figure S3 B). According to the manufacturer, the resin consists of methacrylates and polymethcrylates. Thus first mass loss starting at 200 °C can be attributed to partial loss of the side groups and the second one at 400 °C to depolymerization of the polymer.¹ Water increases the relative importance of the second decomposition step, which can be attributed to partial hydrolysis of the side groups. The decrease in thermal stability causes by organic solvents could be due to extraction of stabilizers from the resin. However, all changes are minor and the IR-spectra are indistinguishable (Figure S3 C), indicating that the bulk of the material remains essentially the same.



Figure S 3: A) TGA-curves for the resins. B) Derivatives of the TGA-curves. Data has been vertically shifted for clarity. C) IR-spectra of the solvent soaked pieces of resin. The curves have been vertically shifted for clarity.

4 Residence time distribution studies in the designed mCOBR

Residence time distribution aided the comparison of the flow condition in the TR and mCOBR. The setup comprises of: Two syringe pumps, one responsible for the oscillatory conditions while the other for the net flow of the fluid through the reactor; A Rheodyne valve, which injects a pulse of inert coloured tracer through the reactor, UV-Vis spectrometer and light source which produce the absorbance spectra of the tracer with change in time. This way the axial dispersion of the tracer in the TR and mCOBR is measured.



Figure S 4 Rig setup for residence time distribution studies. Comprising of two tricontinent syringe pumps, mCOBR, UV-Vis spectrometer, Rheodyne valve and Light source



Figure S 5 Schematic of the design of the oscillatory system employing an immiscible viscous fluid.

Using this technique and by applying eqn 1-4, the E(t) curve, the mean residence time (t_m) and the variance can be obtained from the experimental curves.²

$$E(t) = \frac{C_t}{\int_0^\infty C_t dt}$$
$$t_m = \int_0^\infty t \cdot E(t) dt$$
$$\sigma^2 = \frac{\int_0^\infty (t - t_m)^2 \cdot C(t) dt}{\int_0^\infty C(t) dt}$$

Mixing performance in flow systems of varying configurations can be compared by using the normalised RTD function $E(\theta)$ and the dimensionless time θ :

$$E(\theta) = t_m \cdot E(t)$$
$$\theta = \frac{t}{t_m}$$

Reactor modelling 4.1

The dispersion model satisfactorily describes flows that do not deviate largely from plug flow.² From Fick's Law, molecular diffusion in the x-direction can be expressed mathematically as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Where D is the axial or longitudinal dispersion coefficient, which characterises the degree of back mixing in the flow. In dimensionless form, the differential equation of the dispersion model is as follows:

$$\frac{\partial C}{\partial \theta} = \left(\frac{D}{uL}\right)\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z}$$

Where the dimensionless group, $\left(\frac{\overline{uL}}{uL}\right)$, the vessel dispersion number represents the extent of axial dispersion. The inverse of the dimensionless group is quantified by the Peclet number, Pe, where u is the fluid velocity, and L is the length of the reactor. For ideal mixed flow, the Peclet number is 0 and infinity for an ideal plug-flow.

$$\frac{D}{uL} = \frac{1}{Pe} \rightarrow 0$$

$$\frac{D}{uL} = \frac{1}{Pe} \rightarrow \infty$$
Large dispersion, therefore mixed flow

"Open" boundary conditions, is achieved if the flow is undisturbed at the inlet and outlet of

D

the vessel. In this case the D is same at the boundaries. In the "closed" case, there is a change in flow pattern at the boundaries. The inlet to the reactor is an idealised plug flow, which transforms to a dispersed flow in the reactor and back to plug flow at the reactor exit. The mathematical solution for "open" boundary conditions is given by:

$$E(\theta) = \frac{1}{2} \sqrt{\frac{Pe}{\pi\theta}} e^{\frac{-Pe(1-\theta)^2}{4\theta}}$$

5 mCOBR for silver nanoparticle synthesis

A 0.25 mM solution of AgNO₃ in CH₃CN, and another with 0.75 mM of NaBH₄ and 0.75 g PVP in CH₃CN were pumped with two HPLC pumps (Gilson 305 and Gilson 307) into the prepared reactors with a total flow of 2 mL min⁻¹. Oscillation (0.1 mm and 40 Hz) was induced with a Tricontinent C3000 programmable syringe pump equipped with a 5 mL. The oscillation was generated with an immiscible silicon oil to prevent back mixing of the reagents. A mCOBR and a tubular reactor were employed to generate the nanoparticles. All experiments were performed at room temperature. The formation of the Ag-NPs was monitored by UV-Vis at the outlet of the reactor as a function of time. A back pressure regulator (BPR) was employed to maintain the system under controlled pressure (4 bar). This was done to ensure the HPLC pumps worked adequately. All experiments were run for 100 min. TEM samples were collected after 10 min and 90 min. The synthesized Ag-NP solution was collected in a Duran flask. TEM samples were prepared by diluting a drop of the freshly collected reaction mixture in acetone. A drop of the diluted reaction mixture was dropped onto a carbon-coated copper grid. The so prepared samples were measured in a JEOL 2000FX operated at 200kV.



Figure S 6 Rig setup for Ag-NP synthesis. Comprising of two HPLC pumps, mCOBR, a syringe pump for fluid oscillation, UV-Vis spectrometer, light source and a back-pressure regulator.



6 TEM images and Particle size distribution studies

Figure S 7 TEM-images at the beginning; tubular (left); mCOBR (right)



Figure S 8 Fouling in AM fabricated/3D printed mCOBR and tubular reactors. Fouling is much reduced using optimised conditions in the mCOBR compared to the tubular reactor. Left: Tubular reactor. Centre: mCOBR run under oscillatory conditions. Right: mCOBR run at un-optimised oscillatory conditions.



Figure S 9 Non uniform and/or spherical Ag-NP produced in tubular reactor. White bar corresponds to 20 nm.

Baffled reactor without oscillation:

Reaction conditions and analytics are performed as described in the general procedure, thus no oscillation is induced.



Figure S 10 Ag-NPs obtained in a baffled reactor without oscillation. Left: Picture corresponding to the sample obtained in the reactor without oscillation (left) and under mCOBR conditions (right). Centre: TEM image of the Ag-NP obtained under non-oscillatory conditions. Right: Histogram of the Ag-NPs synthesised under non-oscillatory conditions.

7 UV-Vis spectra of Ag nanoparticles from a regenerated reactor



Figure S 11 UV-Vis of Ag-NPs synthesised in a mCOBR washed with aqua regia (red), compared to that of a solution synthesised with a fresh mCOBR (black).

8 References

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