Supplementary Information

An engineering approach to synthesis of gold and silver nanoparticles by controlling hydrodynamics and mixing based on a coaxial flow reactor

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1 Gold NP synthesis repeatability at various synthesis flow rates

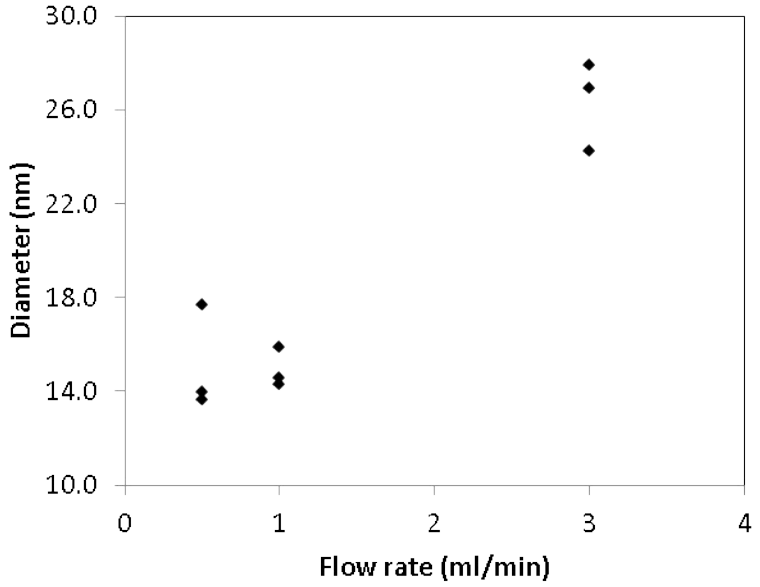

Figure S1: Average diameter of gold NPs synthesized using the CFR with a CFI residence loop at flow rates of 0.5, 1 and 3 ml/min obtained using DCS. Concentration of tetrachloroauric acid, 0.557 mM; concentration of trisodium citrate, 0.09 M; volumetric flow rate ratio, 32.3 : 1 (Q_{out} : Q_{in}, $HAuCl_4$: Na_3citrate); molar flow rate ratio, 1 : 5 ($HAuCl_4$: Na_3citrate); temperature, 80 °C.

2 High magnification images of gold NPs synthesised at various flow rates

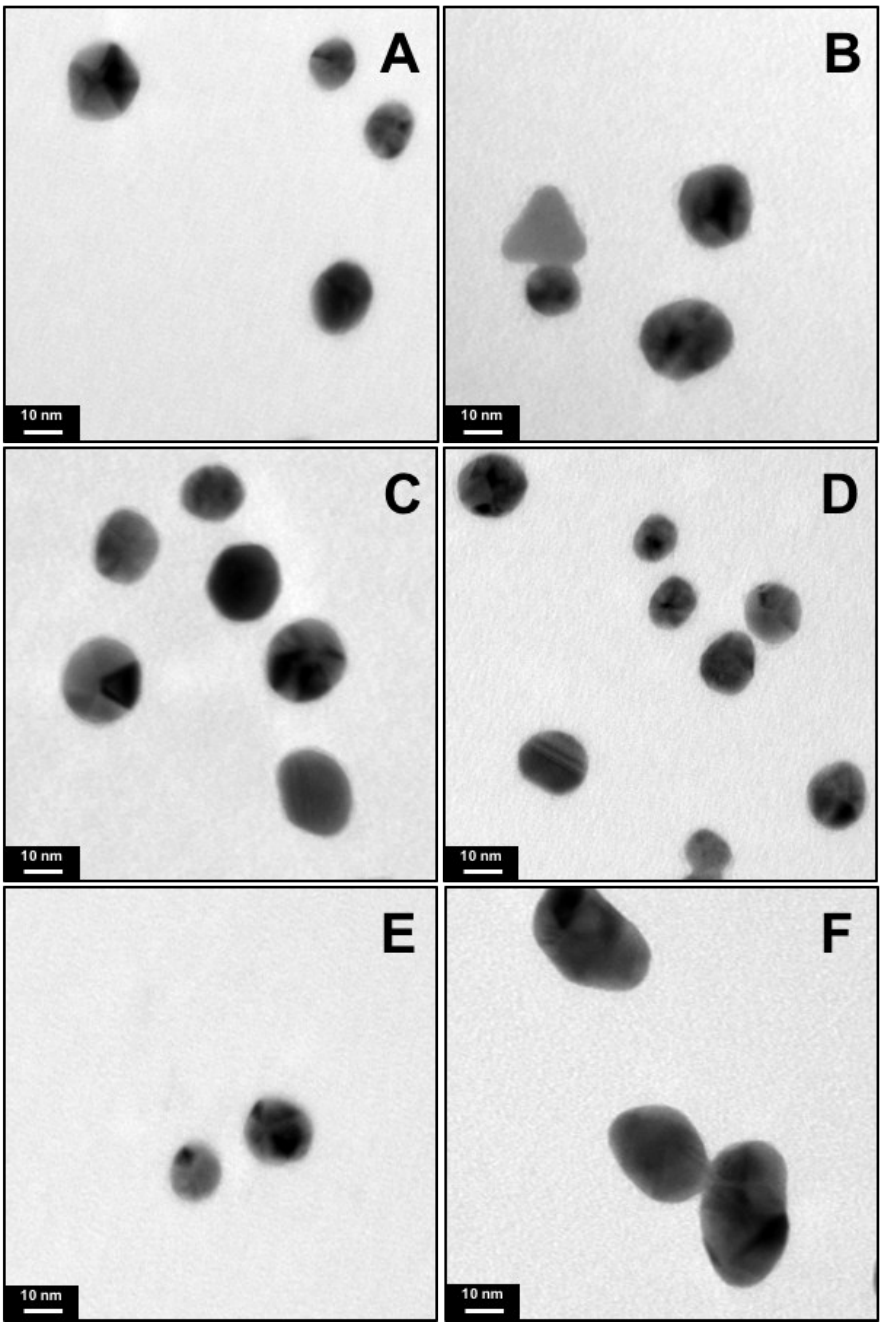

Figure S2: High magnification TEM images of gold NPs synthesized using the CFR with a CFI residence loop at a total flow rate of A: 0.25 ml/min, B: 0.5 ml/min, C: 0.75 ml/min, D: 1 ml/min, E: 1.5 ml/min and F: 3 ml/min. Concentration of tetrachloroauric acid, 0.557 mM; concentration of trisodium citrate, 0.09 M; volumetric ratio, 32.3: 1 (Q_{out} : Q_{in}, $HAuCl_4$: Na_3citrate); molar flow rate ratio, 1 : 5 ($HAuCl_4$: Na_3citrate); temperature, 80 °C.

3 Number concentration of gold NPs synthesised at various flow rates

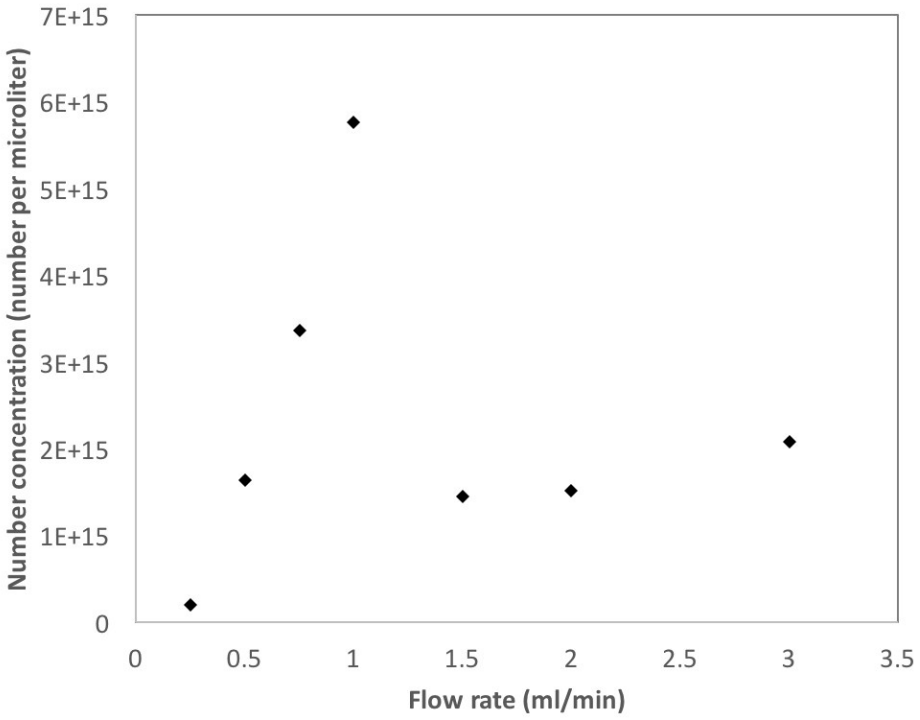

Figure S3: Number concentration of gold NPs synthesized using the CFR with a CFI residence loop at a total flow rate of 0.25-3 ml/min, obtained from DCS. Concentration of tetrachloroauric acid, 0.557 mM; concentration of trisodium citrate, 0.09 M; volumetric ratio, 32.3 : 1 (Q_{out} : Q_{in}, $HAuCl_4$: Na_3citrate); molar flow rate ratio, 1 : 5 ($HAuCl_4$: Na_3citrate); temperature, 80 °C.

4 Gold NP synthesis repeatability at various synthesis temperatures

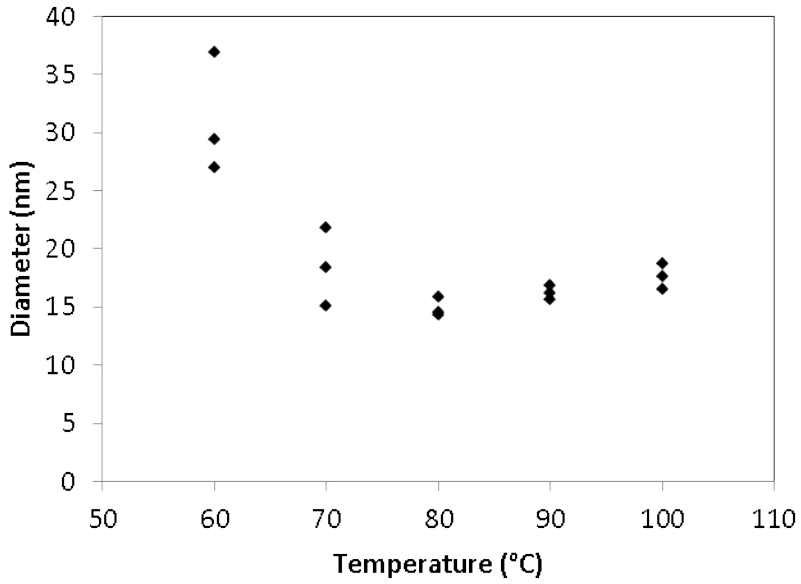

Figure S4: Average diameter of gold NPs synthesized using the CFR with a CFI residence loop at temperatures between 60-100 °C obtained using DCS. Concentration of tetrachloroauric acid, 0.557 mM; concentration of trisodium citrate, 0.09 M; volumetric flow rate ratio, 32.3 : 1 (Q_{out} : Q_{in}, $HAuCl_4$: Na_3citrate); molar flow rate ratio, 1 : 5 ($HAuCl_4$: Na_3citrate); flow rate, 1 ml/min.

5 Visualisation of flow in the CFR at high Reynolds number

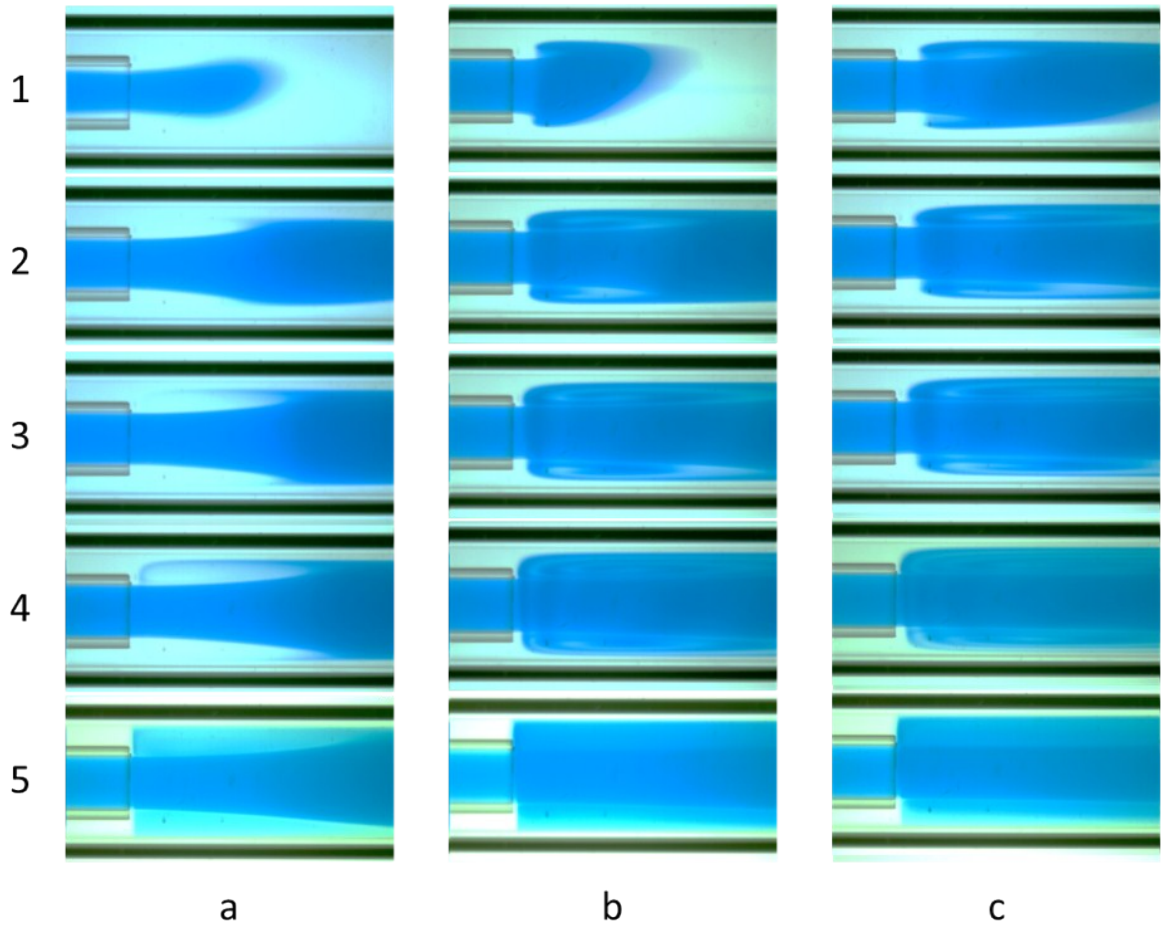

Figure S5: Flow visualization in the CFR with an inner tube I.D. of 0.798 mm at different Reynolds numbers: a) 5.1 ml/min (Re inner tube, 132, Re main channel, 54), b) 10.1 ml/min (Re inner tube, 265, Re main channel, 107), c) 15.1 ml/min (Re inner tube, 397, Re main channel, 160). Basic blue dye was pumped through the inner tube between 5 and 15 ml/min and water was pumped through the outer tube at a fixed flow rate of 0.1 ml/min. Picture "1" is taken when the dye is initially pumped through the inner tube with increasing numbers taken at later times. Picture "5" is taken at steady state. Flow direction is from left to right.

6 Silver NP synthesis repeatability with inner tube I.D. variation

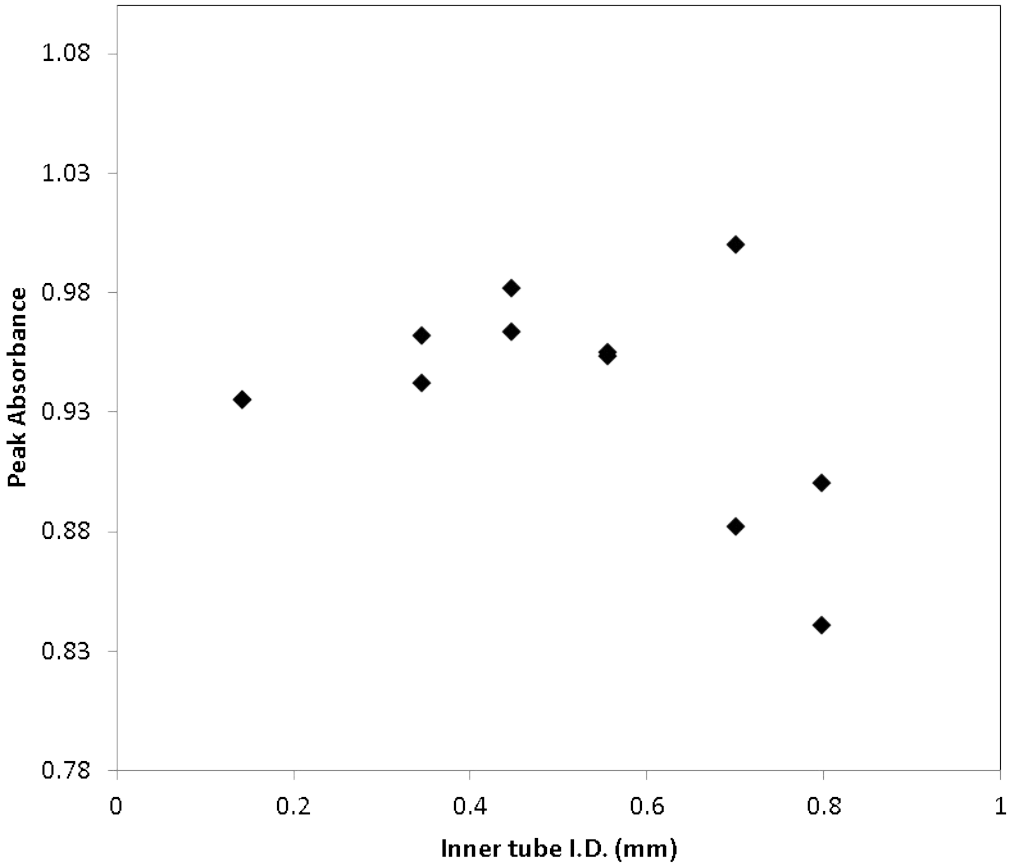

Figure S6: Peak absorbance obtained from UV-Vis spectra vs. inner tube internal diameter of repeat experiments for silver NPs synthesized using the CFR. Concentration of silver nitrate, 0.1 mM; concentration of sodium borohydride, 0.3 mM; concentration of trisodium citrate, 0.5 M; volumetric flow rate ratio, 1 : 1 (Q_{out} : Q_{in}, $NaBH_4$: $AgNO_3$); molar flow rate ratio, 1 : 3 : 5 ($AgNO_3$: $NaBH_4$: Na_3citrate); flow rate, 1 ml/min, temperature 22 – 24 °C.

7 CFD model of silver nitrate reaction within the CFR

To investigate how the silver nitrate concentration is affected at the outlet of the reactor when the inner tube I.D. is varied, a CFD model of the CFR was developed and solved using COMSOL Multiphysics software. Using a 2D axisymmetric geometry, the real geometry of the CFR was implemented into the model, using a length from the inner tube outlet to the outlet of the CFR of 130 mm. The inner tube I.D. and wall thickness was varied according to the inner tubes used in the experiment. The model implemented laminar flow physics for the calculation of the velocity profile within the channel, and transport of diluted species for the diffusion and reaction of reagents. COMSOL uses the following equations to solve the velocity profile:

$$\rho\frac{\partial u}{\partial t} + \rho u\nabla u = -\nabla p + \nabla\left(\mu\left(\nabla u + (\nabla u)^T\right) - \frac{2}{3}\mu(\nabla u)I\right) + \rho g$$

$$\frac{\partial \rho}{\partial t} + \nabla(\rho u) = 0$$

Where:

ρ = density [kg/m^3]

u = velocity vector [m/s]

p = pressure [Pa]

μ = dynamic viscosity [Pa.s]

T = temperature [K]

I = identity matrix

g = gravitational field [m/s^2]

The following equations were used to solve the concentration profile

$$\frac{\partial c_i}{\partial t} + u\nabla c_i = \nabla\left(D_i\nabla c_i\right) + R_i$$

$$N_i = -D_i\nabla c_i + uc_i$$

Where:

c is the concentration of species i [mol/m^3]

D is the diffusion coefficient of species i [m^2/s]

R is the reaction rate expression of species i [mol/(m^3.s)]

N is the molar flux of species i [mol/(s.m^2)]

No-slip boundary conditions at the walls of the channel were used and the outflow was set to zero pressure. Diffusive flux at the outflow was also set to zero. The reaction rate was assumed to be first order with respect to silver nitrate and first order with respect to sodium borohydride to take the form $r = kC_{AgNO_3}C_{NaBH_4}$. The reaction rate constant was

assumed to be 2 x 10^4 l/mol.s. This was chosen to represent a fast reaction, (fast in comparison to the mixing time achievable in the CFR using the conditions tested experimentally, where the primary mechanism of mass transport is diffusion) and although this is an unknown quantity it is suggested that reactions involving silver NP formation are fast according to the literature. Polte *et al*. suggest reduction of silver occurs in less than 200 ms,[1] and Takesue *et al*. observed nucleation of silver NPs in less than 1 ms.[2] The diffusion coefficient used for silver nitrate was 1.718 x 10^{-9} m^2/s,[3] and for sodium borohydride was 3.5 x 10^{-9} m^2/s.[4] Figure S7 shows typical concentration profiles of silver nitrate, sodium borohydride and reduced silver at the inlet and outlet of the CFR. Figure S8 shows the silver nitrate concentration at the outlet of the reactor for different inner tube I.D. The results show an increase in silver nitrate concentration with increasing inner tube I.D. Since the volumetric flow rate ratio used was 1 : 1 (Q_{in} : Q_{out}), the inner stream expands after the outlet of the inner tube.

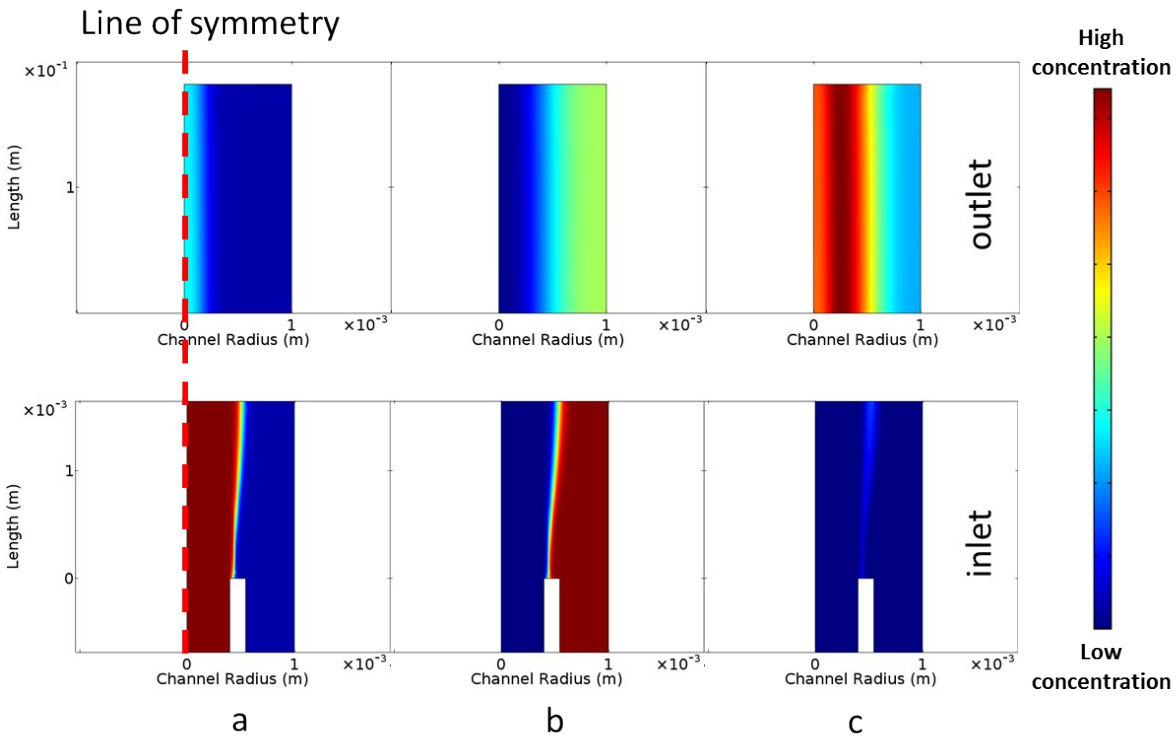

Figure S7: Concentration maps in the CFR after simulating reaction between silver nitrate and sodium borohydride to produce reduced silver at a flow rate of 1 ml/min using a 0.798 mm inner tube I.D. Bottom row shows concentrations at the inlet region of the inner tube and top row at the outlet region of the outer tube for a) silver nitrate, b) sodium borohydride and c) reduced silver.

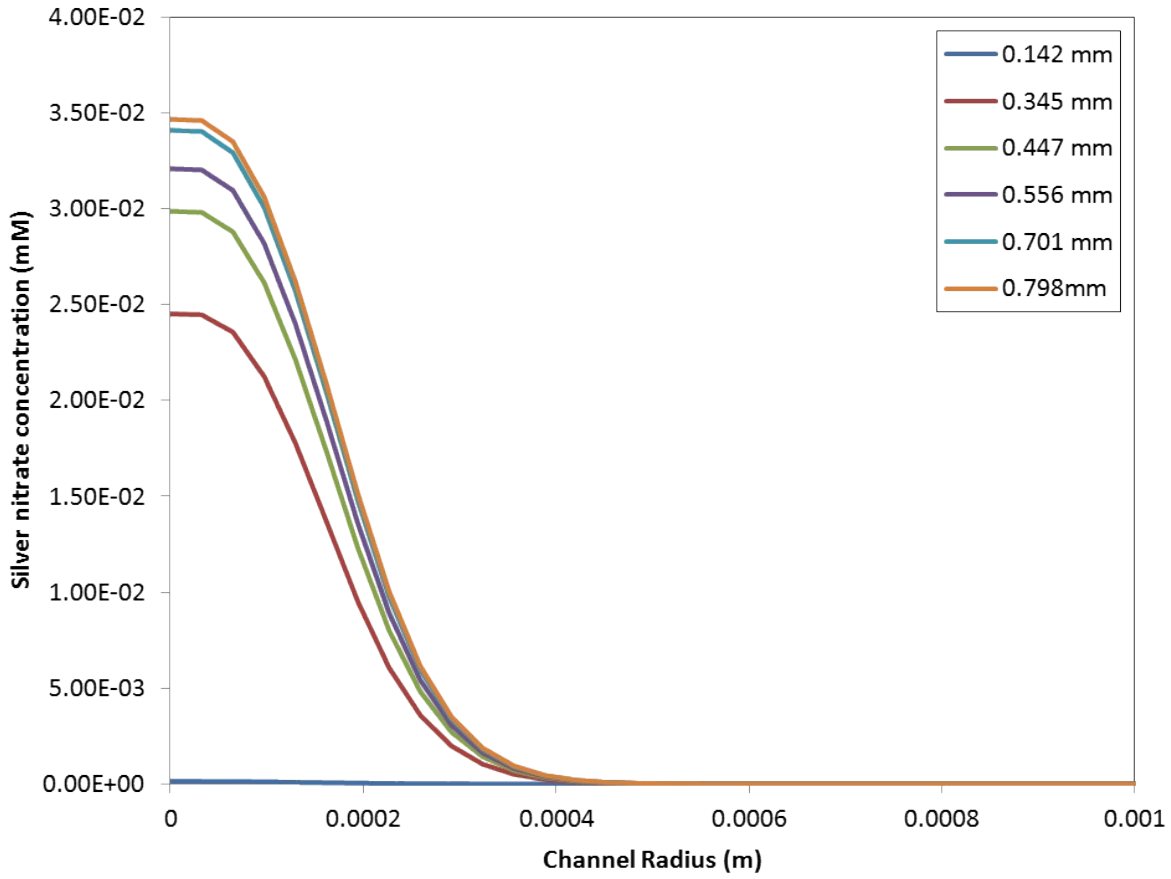

Figure S8: Silver nitrate concentration profiles at the outlet of the CFR for various inner tube I.D. Concentration of reagents were: silver nitrate 0.1 mM, trisodium citrate 0.5 mM, sodium borohydride 0.3 mM. A flow rate ratio of 1 : 1 $AgNO_3$ to $NaBH_4$ was fixed at a flow rate of 1 ml/min at room temperature (298 K).

References

1. Polte, J.; Tuaev, X.; Wuithschick, M.; Fischer, A.; Thuenemann, A. F.; Rademann, K.; Kraehnert, R.; Emmerling, F., Formation Mechanism of Colloidal Silver Nanoparticles: Analogies and Differences to the Growth of Gold Nanoparticles. *ACS Nano* **2012,** *6* (7), 5791-5802.
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3. Harned, H. S.; Hildreth, C. L., The Diffusion Coefficient of Silver Nitrate in Dilute Aqueous Solution at 25°. *J Am Chem Soc* **1951,** *73* (7), 3292-3293.
4. Chatenet, M.; Molina-Concha, M. B.; El-Kissi, N.; Parrour, G.; Diard, J. P., Direct rotating ring-disk measurement of the sodium borohydride diffusion coefficient in sodium hydroxide solutions. *Electrochimica Acta* **2009,** *54* (18), 4426-4435.