Supporting Information

Size Controlled Flow Synthesis of Gold Nanoparticles using a Segmented Flow Microfluidic Platform

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Two-phase Taylor flow characterization

The phase distribution in two-phase flow is characterized by the hold-up ε_d (defined for the dispersed phase)

$$\varepsilon_d = \frac{V_d}{V_d + V_c},$$

where V_i denotes the volume occupied by the dispersed and continuous phase.

In Taylor flow, the local flow velocity of the two phases is different, which is related via the two-phase slip s, which represents the ratio of the local flow velocities w_i according to

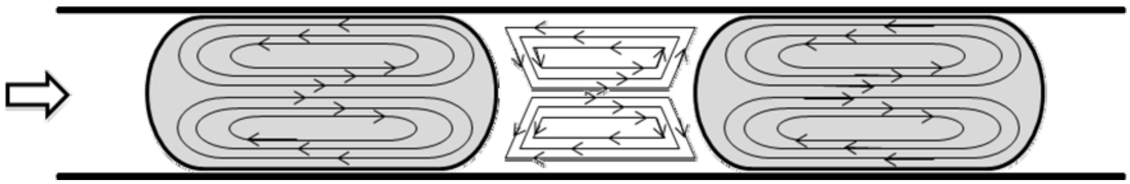
$$s = \frac{w_d}{w_c}.$$

It is convenient to define the slip velocity v_S, which is estimated using standard ways as

$$v_S = \frac{u_d}{\varepsilon_d} - \frac{u_c}{1-\varepsilon_d},$$

where u_d and u_c are the superficial velocities of the dispersed and continuous fluids, respectively. Thus, the slip velocity is the difference between the velocity of the two phases. The higher the slip velocity, the better is the circulation in the reactor. An increase in viscosity of any of the phase would enhance the frictional forces between the two fluids and thereby reduce the slip velocity. Thus, with reduced slip velocity the extent of circulation in the slugs would decrease.

In terms of nomenclature, internal circulation occurs in both the slugs, continuous as well as dispersed phase. Clearly two circulation zones are formed in the slugs (as shown in the scheme below). Thus, ‘internal circulation’ describes a phenomenon, while ‘recirculation zones’ are the physical flow zones that lead to internal circulation.



Film thickness and slug length calculations

Typically, for the case of cylindrical microchannels, the film thickness is estimated using Bretherton's correlation, which is given in terms of the channel diameter and the flow Capillary number

$$\mathrm{Ca} = \frac{u\mu}{\sigma},$$

where u is the continuous phase superficial velocity, μ is the continuous phase dynamic viscosity, and σ is the interfacial tension.

For the case of square capillaries, the film thickness at the diagonally opposite corners and over the flat channel sides differs. It is known that Bretherton's correlation for the film thickness δ and its analogues are valid for the estimation of film thickness at the side walls of square capillaries, thus we use it for our calculations:

$$\delta = 0.66d\mathrm{Ca}^{0.66},$$

where d denotes the hydraulic diameter.

We can also calculate the two-phase Weber number We, which is defined as

$$\mathrm{We} = \frac{du^2\rho}{\sigma},$$

where d denotes the hydraulic diameter, u is the continuous phase superficial velocity, ρ is the continuous phase density, and σ is the interfacial tension. The values of the Capillary and Weber number with respect to the two-phase system and the wall wettability are given in Table S1.

The calculated film thickness subject to the two-phase Weber number is depicted in Figure S1.

Table S1. **Capillary and Weber number depending on the two-phase system, residence time, and microchannel wall wettability.**

Hydrophilic microchannel

	mean residence time [s]	Capillary number	Weber number
Air - water	10	1.83E-05	5.16E-04
	20	9.14E-06	1.29E-04
	40	4.57E-06	3.22E-05
Toluene - water	10	6.89E-03	9.72E-02
	20	3.45E-03	2.43E-02
	40	1.72E-03	6.08E-03
Silicone oil - water	10	2.86E-02	4.04E-01
	20	1.43E-02	1.01E-01
	40	7.16E-03	2.53E-02

Hydrophobic microchannel

	mean residence time [s]	Capillary number	Weber number
Air - water	10	1.83E-05	5.16E-04
	20	9.14E-06	1.29E-04
	40	4.57E-06	3.22E-05
Toluene - water	10	1.68E-01	7.39E-02
	20	8.40E-02	1.85E-02
	40	4.20E-02	4.62E-03
Silicone oil - water	10	8.45E-03	3.47E-01
	20	4.23E-03	8.69E-02
	40	2.11E-03	2.17E-02

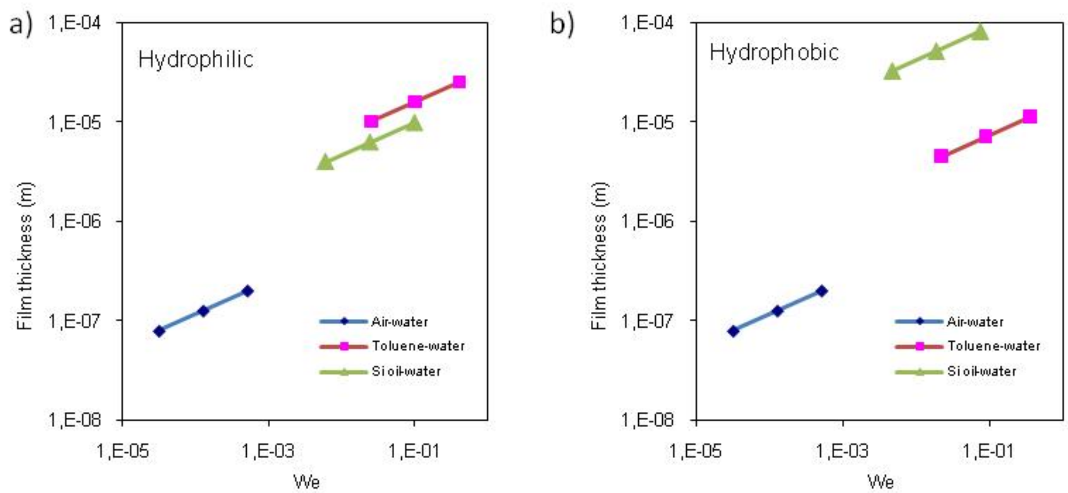


Figure S1. **Estimation of film thickness in air-water, oil-water and toluene-water systems: a) hydrophilic microchannel reactor b) hydrophobic microchannel reactor.**

Having obtained the film thickness we can also estimate the dispersed slug length *L*. Therefore we apply in a first step a correlation to calculate the equivalent radius of a dispersed spherical droplet R_{sphere} based on the Weber number We, which reads

$$R_{sphere} = -0.1276 d \ln\left[\frac{\mathrm{We}(1-\varepsilon)}{(\mathrm{We}\varepsilon)^{0.15}}\right] + 0.5595$$

where *d* denotes the hydraulic diameter, and ε the dispersed phase fraction.

This allows the computation of the dispersed spherical droplet volume

$$V_{sphere} = \frac{4}{3}\pi R_{sphere}^3 .$$

In the microchannel, the dispersed slug can be assumed to have a cylindrical shape, with the radius $R_{cylinder}$ given by the difference between the hydraulic diameter and the film thickness

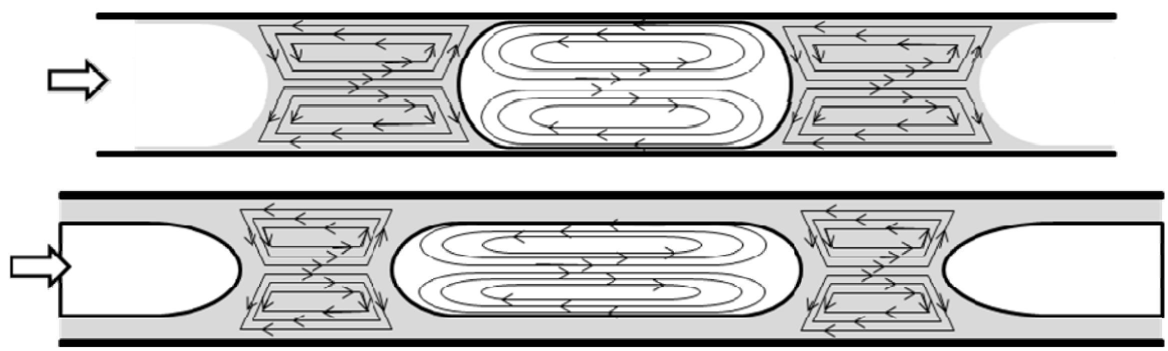
$$R_{cylinder} = \frac{d}{2} - \delta.$$

Thus we can estimate the dispersed slug length L as

$$L = \frac{V_{sphere}}{\pi R_{cylinder}^2}.$$

Figure S2 depicts the obtained slug length depending on the residence time for the hydrophilic and hydrophobic microchannel.

The scheme below illustrates the connection between film thickness and slug length, a higher film thickness reduces the radial space for the dispersed phase slugs, and will hence lead to longer slugs.



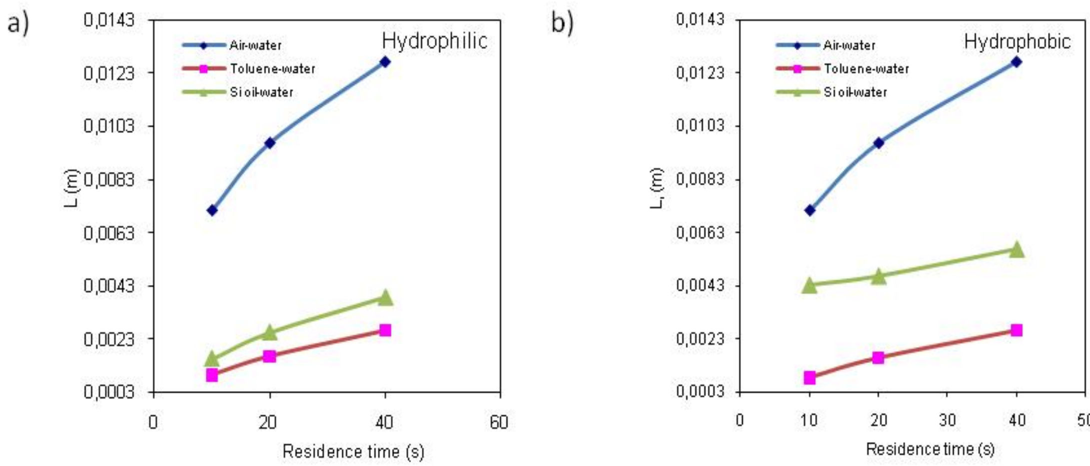


Figure S2. **Estimation of the slug length in air-water, oil-water and toluene-water systems: a) hydrophilic microchannel reactor b) hydrophobic microchannel reactor.**

Role of dispersion for hydrophobic microchannels

To elucidate the role of dispersion we switched the wetting behavior of the microchannel by applying a PTFE coating. Thus the reacting aqueous phase is switched from being the continuous phase to being dispersed in the inert carrier. The resulting particle size distributions are plotted in Figure S3.

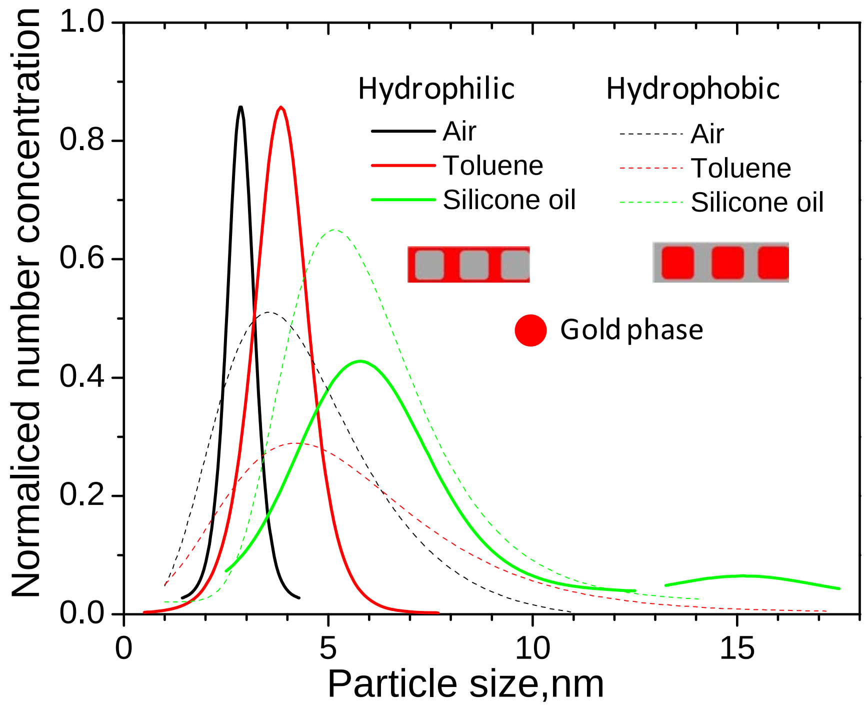


Figure S3. **Particle size distribution diagram from AuNPs obtained in silicone oil/toluene/air-aqueous segmented flow at Rt = 10 s using a hydrophobic microchannel, [Au]= 1 mM.**