Supporting Information (Part 1):

Determination of the Exact Particle Radius Distribution for Silica Nanoparticles via Capillary Electrophoresis and Modelling the Electrophoretic Mobility with a Modified Analytic Approximation

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Part 1: TEM and TDA Data

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Section S1. Moment Analysis

For a given distribution (*e.g.*, assuming a recorded eluted peak, c = f(t), c = concentration, t = time) the following moment equations are valid ($n \in \{0,1,2,3,\ldots\}$):

$$m_n = \int_0^\infty c\, t^n\, dt \qquad (m_n = n^{th} \text{ moment about the origin}) \qquad (S1.1)$$

$$\mu_n = \frac{m_n}{m_0} = \frac{\int_0^\infty c\, t^n\, dt}{\int_0^\infty c\, dt} \qquad (\mu_n = n^{th} \text{ absolute moment}) \qquad (S1.2)$$

$$\mu'_n = \frac{\int_0^\infty c\, (t-\mu_1)^n\, dt}{\int_0^\infty c\, dt} \qquad (\mu'_n = n^{th} \text{ central moment}) \qquad (S1.3)$$

These moments can be calculated numerically for any distribution. The integral m_0 is identical with the peak area. The first absolute moment μ_1 corresponds to the mean. The second central moment μ'_2 is the variance σ^2. Additional quantities, which can be calculated are the skewness S and the kurtosis K. The excess E quantifies the deviation of K from that of a Gaussian normal distribution.

$$S = \frac{\mu'_3}{\sqrt{(\mu'_2)^3}} \qquad \text{(standardized third central moment)} \qquad (S1.4)$$

$$W = \frac{\mu'_4}{(\mu'_2)^2} \qquad \text{(standardized forth central moment)} \qquad (S1.5)$$

$$E = W - 3 \qquad \text{(3 is the kurtosis of a normal distribution)} \qquad (S1.6)$$

If S = 0 and E = 0, then there is no deviation from a Gaussian normal distribution.

Section S2. TDA: Theoretical Background, Measurement Conditions and Data Evaluation

In 1953 Taylor [I] has shown that a plug of solute (with assumed infinitely short length), which is pumped at constant volume rate through a tube of circular cross-section under laminar flow will be broadened so that the final concentration distribution will be symmetrical about the mean, provided several boundary conditions are fulfilled [II]. This final concentration distribution will be given by a Gaussian function (<c> = f(x), <c> = radially averaged concentration, x = distance), as if the dispersion were only effected by axial molecular diffusion, although it is due to the coupling of a radial symmetric velocity inhomogeneity with radial diffusion. Mass transport by axial diffusion is regarded by him to be negligible. Taylor has therefore spoken of a "virtual coefficient of diffusivity" K, which is given by:

$$K = \frac{a_c^{\,2} < v >^2}{48\, D_c} \qquad \text{(S1.7)}$$

where: a_c = radius of capillary, <v> = mean linear velocity, D_c = collective diffusion coefficient

Later Aris [III] has added that it is not required to neglect axial diffusion, because with eliminated higher moments the total variance is the sum of the partial variances:

$$K = D_c + \frac{a_c^{\,2} < v >^2}{48\, D_c} \qquad \text{(S1.8)}$$

For a trace recorded at a distance x, if the conditions for a Taylor-Aris distribution are given (*cf.*, Section S3), the collective diffusion coefficient D_c can be calculated from the variance of the function <c> = f(t) with <c> = radially averaged concentration, t = time, and $\sigma_t^2 = 2Kt$ (σ_t^2 = variance). If D_0 (the diffusion coefficient at infinite dilution) can be approximated by D_c, then D_c is directly related to the hydrodynamic radius r_H *via* the Stokes-Einstein equation.

I Taylor, G. Dispersion of soluble matter in solvent flowing slowly through a tube, *Proc. R. Soc. London A*, **1953**, *219*, 186-203.

II Taylor, G. Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion, *Proc. R. Soc. London A*, **1954**, *225*, 473-477.

III Aris, R. On the dispersion of a solute in a fluid flowing through a tube, *Proc. R. Soc. London A*, **1955**, *235*, 67-77.

We determined the mean hydrodynamic radius r_H with following procedure: after filling the capillary with borate buffer of defined concentration, the sample (diluted with borate buffer of identical concentration) was pumped at a constant pressure difference (Δp = 14 mbar) through a fused-silica capillary (T = 25 °C). The detection wavelength was set to 200 nm. All measurements were made with a capillary of 75 μm I.D. of appropriate length, which provides a maximum signal height without (at the selected mean velocity of the liquid) exceeding the validity range of the Taylor-Aris equation (*cf.*, Section S3). Absence of adsorption of the particles onto the capillary wall was confirmed by comparing the inflection point of the concentration profile (elution time) with that of the nonadsorbed monomolecular substance thiourea (no time shift) and by fitting the ascending part of the recorded trace to a cumulative Gaussian function (no apparent asymmetry). The recorded absorbances were within the linearity range of the detector (data not shown).

All traces (apparent absorbance A = f(t)) were fitted to the cumulative Gaussian function by non-linear regression (see Figure S3 and Table S1):

$$A_{(t)} = \frac{1}{\sigma_t \sqrt{2\pi}} \int_0^t e^{-\frac{(t-t_H)^2}{2\sigma_t^2}} dt \qquad \text{(S1.9)}$$

where $A_{(t)}$ = apparent absorbance, t = time, t_H = inflection point, σ_t = width of the distribution.

Hydrodynamic radii r_H were calculated from the obtained diffusion coefficients by applying the Stokes-Einstein equation. Results obtained via Taylor equation do not deviate significantly from those obtained via Taylor-Aris equation (refer to Table S1).

Section S3. Validity Range of the Taylor-Aris Equation

Requirements for the validity of the Taylor-Aris equation were investigated by Belongia and Baygents [IV]:

$$\tau = \frac{D_c \, t_H}{a_c^{\,2}} > 10 \qquad \text{(S1.10)}$$

where: τ = characteristic diffusion time, D_c = collective diffusion coefficient, t_H = elution time (inflection point of recorded curve), a_c = radius of capillary.

While a_c is fixed at 38 μm, following values have to be given for the diffusion coefficients at 25 °C (values taken from results of TDA analysis): D_c(SNP12) = $30 \cdot 10^{-12}$ m^2 s^{-1} and D_c(SNP22) = $15 \cdot 10^{-12}$ m^2 s^{-1}. The time t_H depends on the length of the capillary (as the pressure difference was kept constant, refer to Table S1): t_H = 18 min.

With this data set, we obtain the following results:

τ(SNP12) = 22.4

τ(SNP22) = 11.2.

This calculation shows that under the conditions of the measurements of the traces shown in Figure S3 the requirements for the validity of the Taylor-Aris equation are fulfilled. No deviation of the results obtained via Taylor equation from those obtained via Taylor-Aris equation (refer to Table S1) confirms the additional validity of the Taylor equation. There is no significant influence of axial diffusion (taken into consideration with the first term of the Taylor-Aris equation, Equation S1.8) on the obtained result.

[IV] Belongia, B. M.; Baygents, J. C. Measurements on the Diffusion Coefficient of Colloidal Particles by Taylor-Aris Dispersion, *J. Colloid Interface Sci*. **1997**, *195*, 19-31

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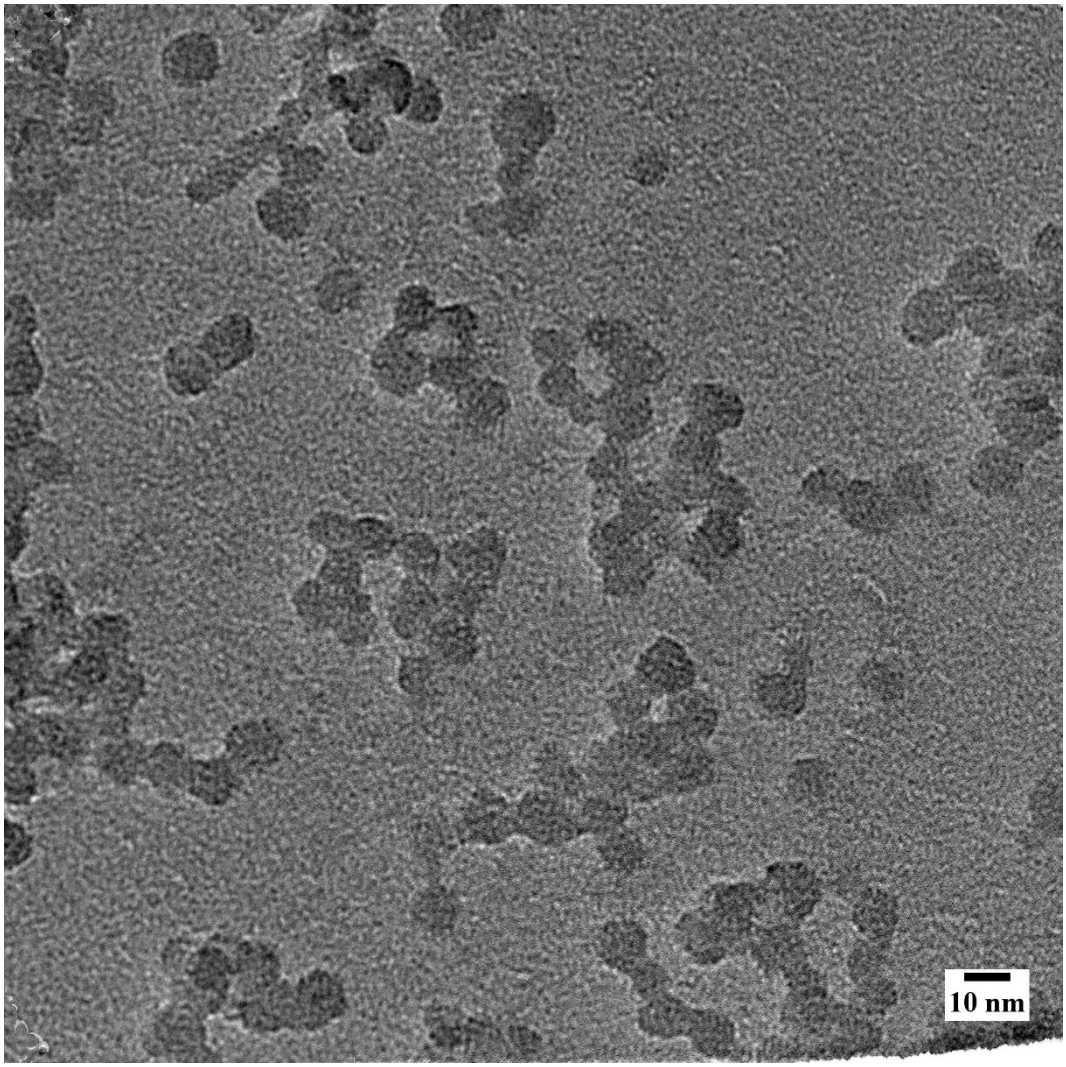

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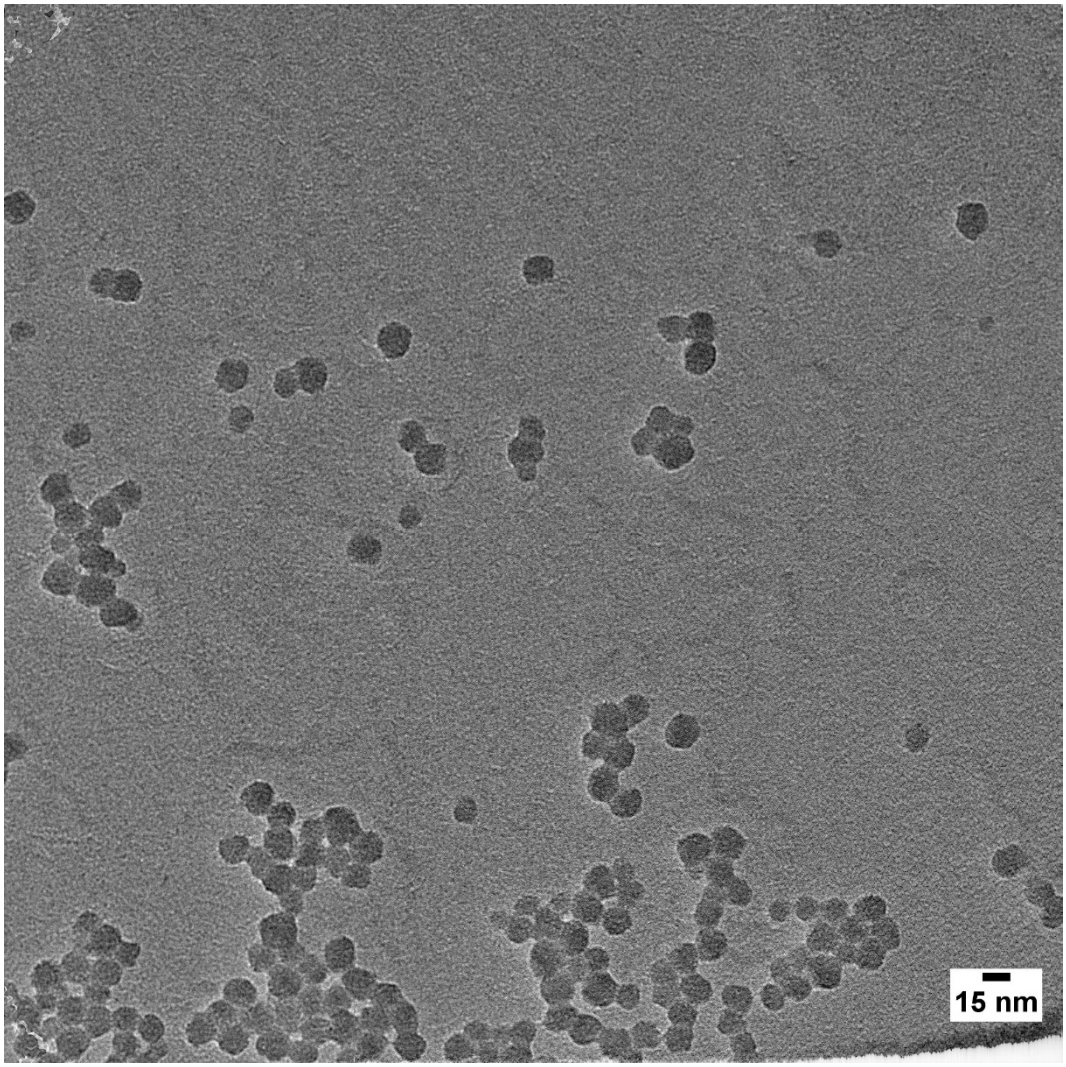

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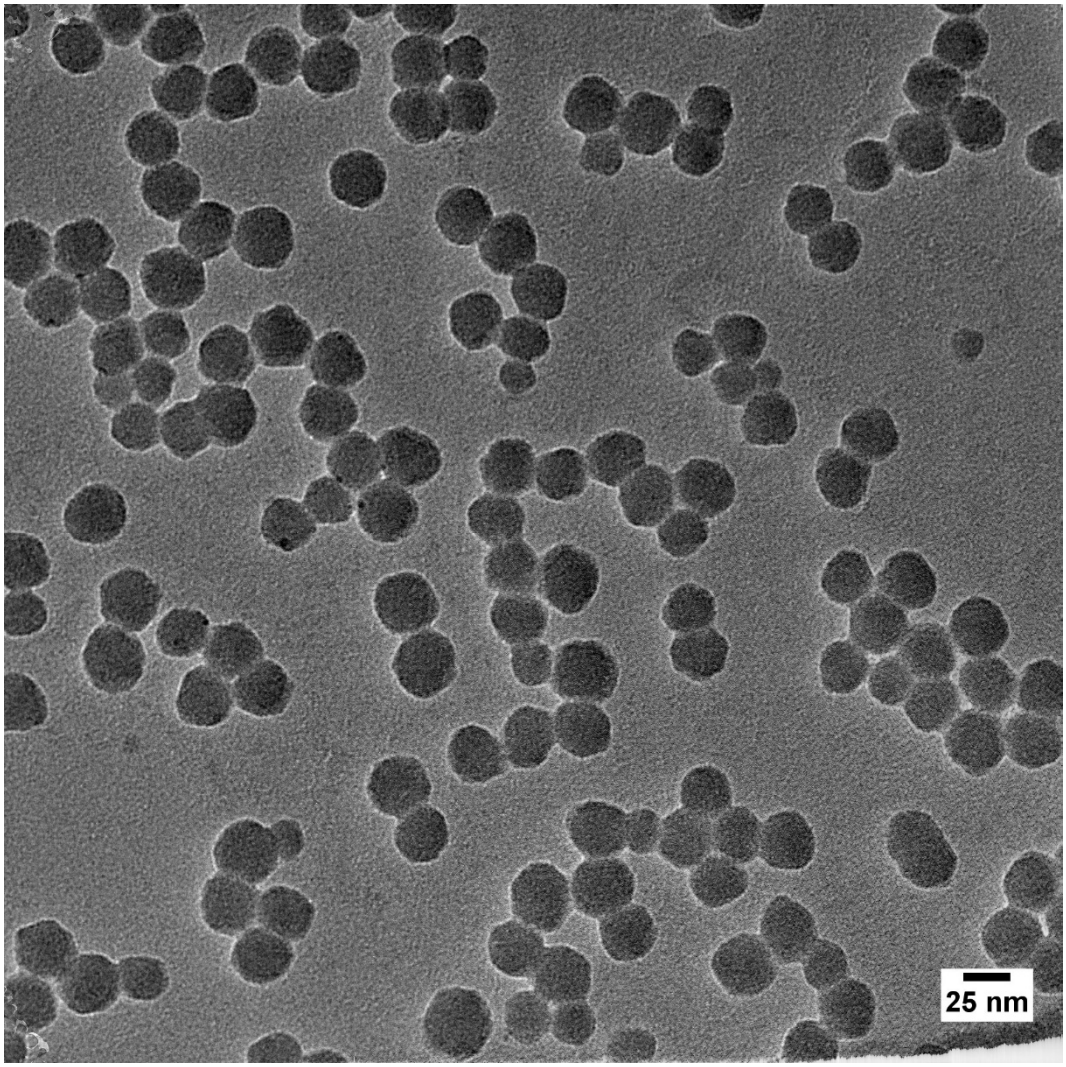
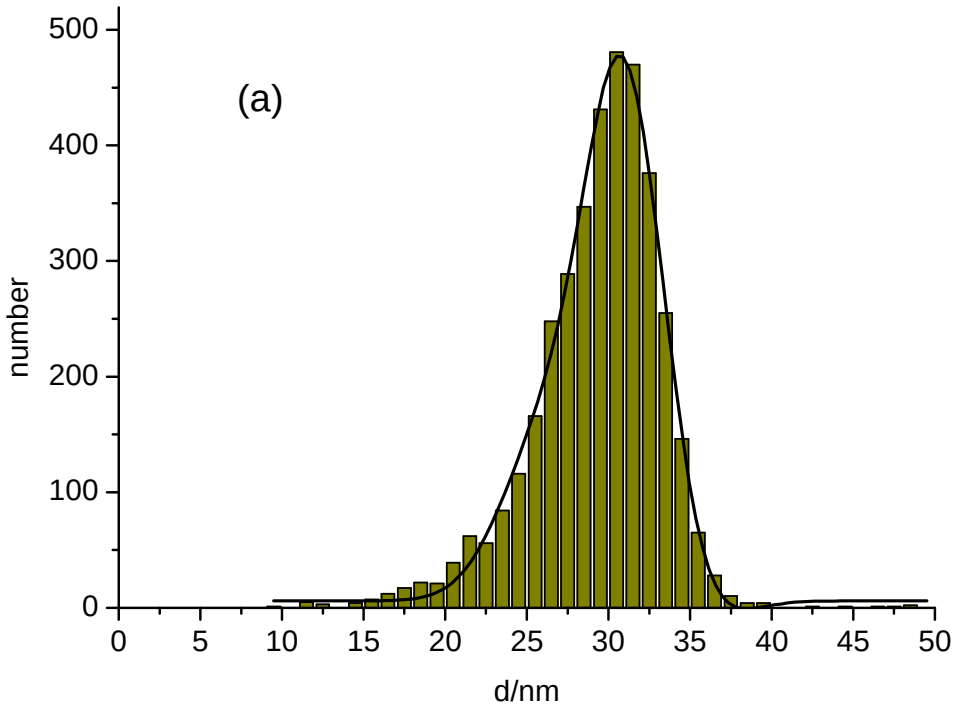


Figure S1. TEM micrographs for (a) SNP7, (b) SNP12, and (c) SNP22.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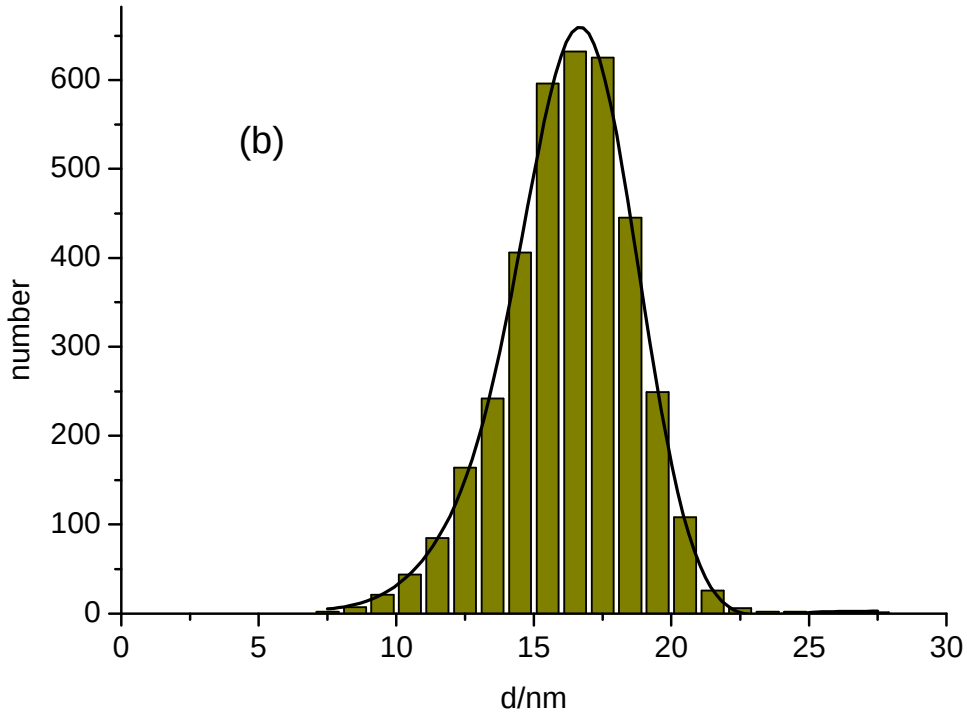
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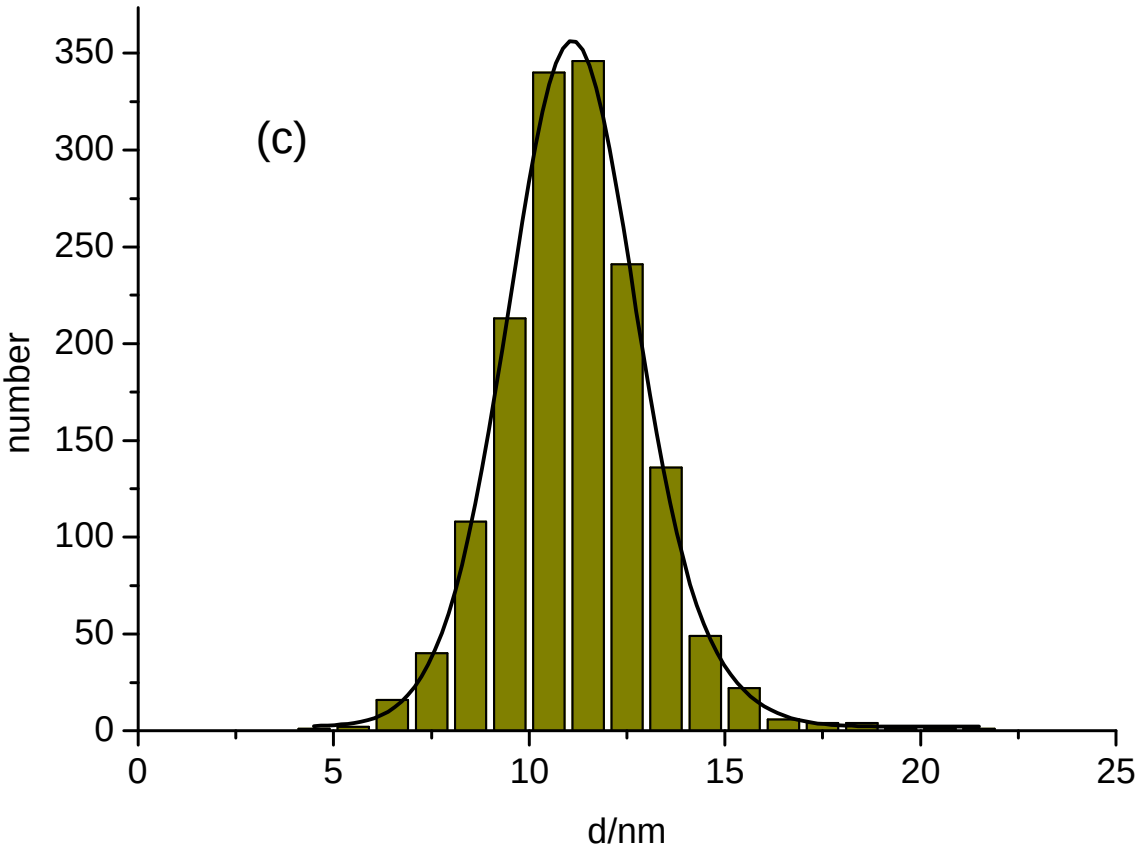
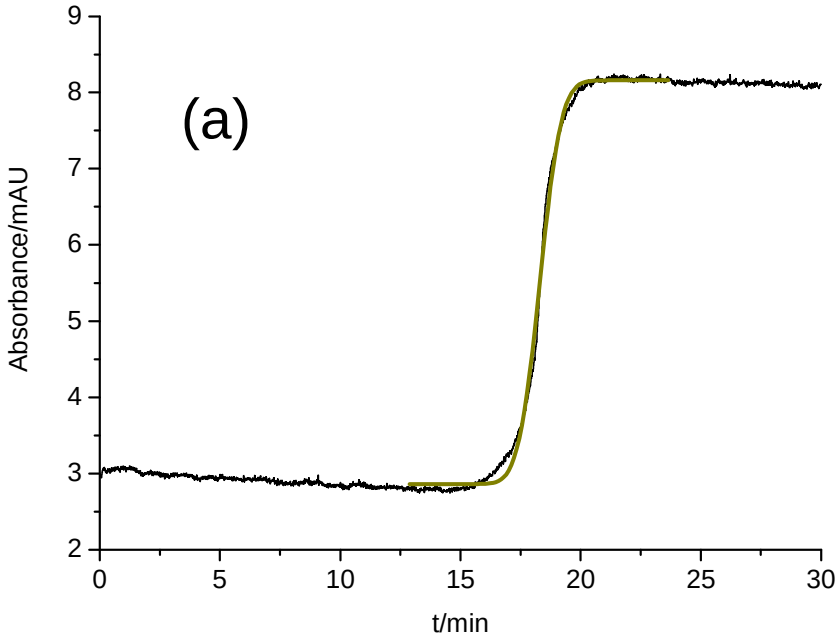


Figure S2. Fitting of TEM data for (a) SNP 22, (b) SNP 12, and (c) SNP 7 to a Gram-Charlier series of type A.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Absorbance/mAU
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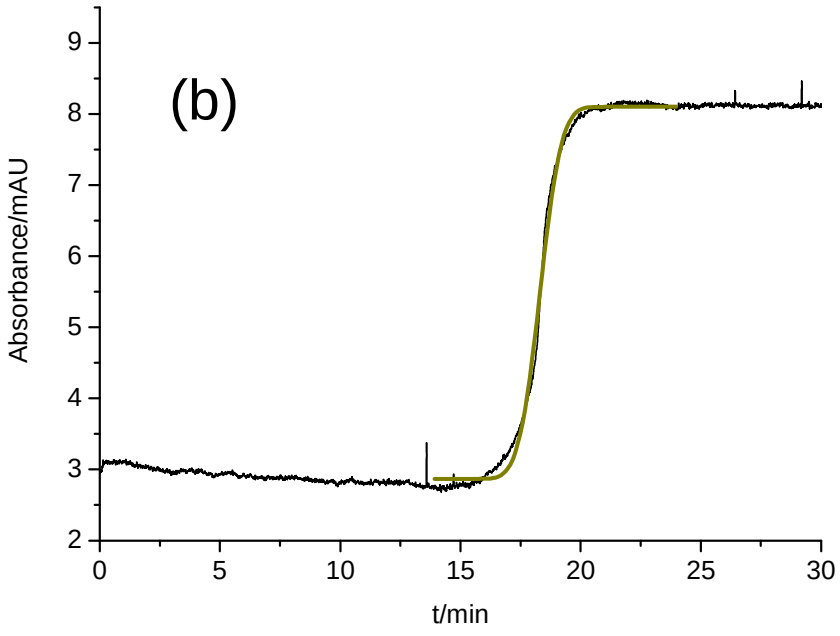
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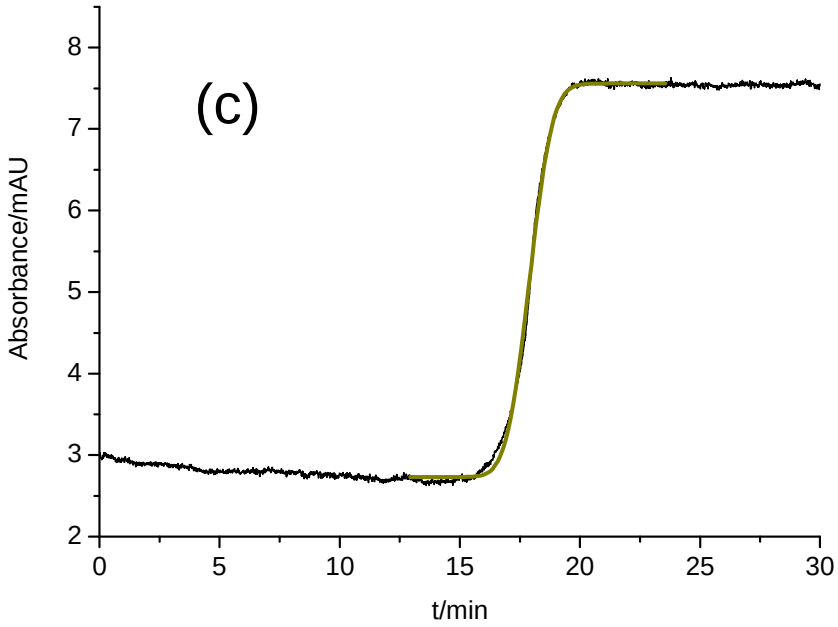
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Absorbance/mAU
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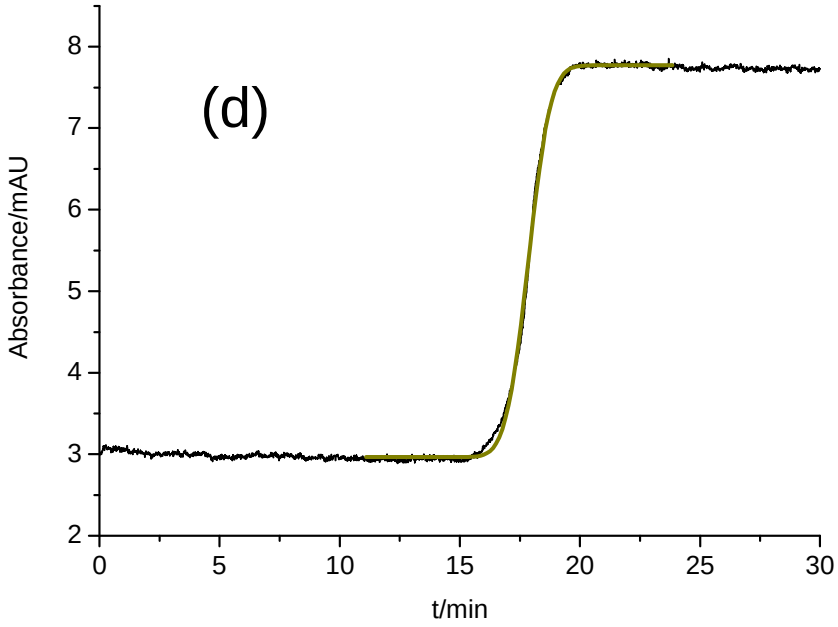
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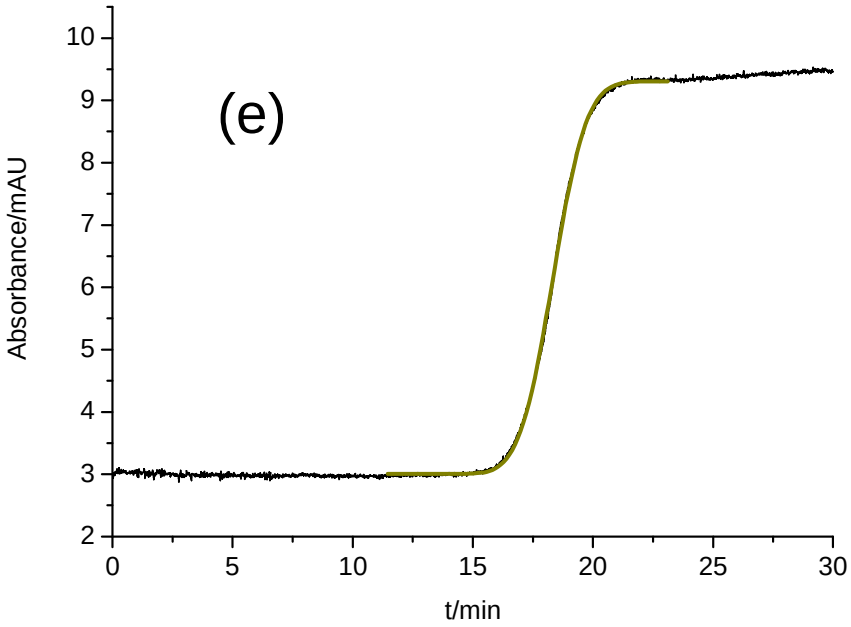
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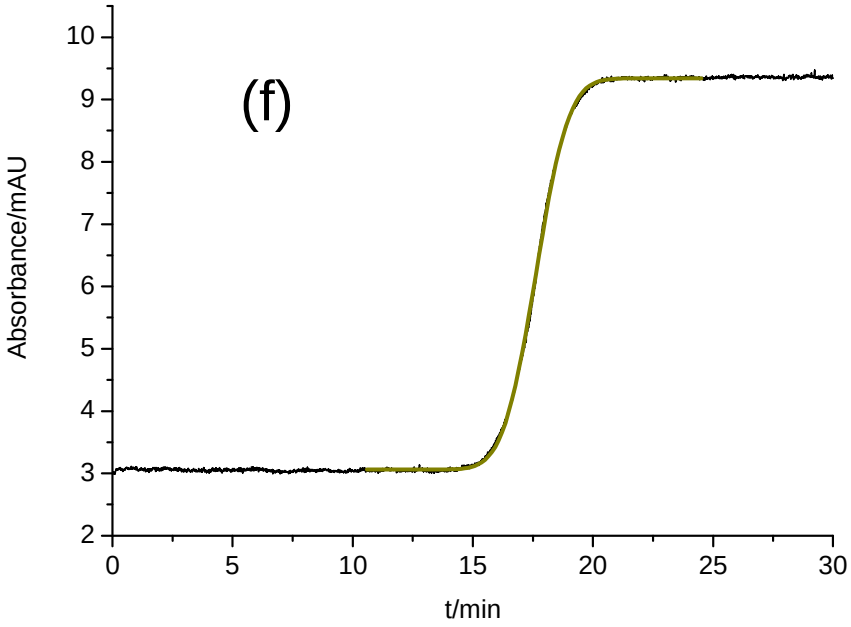
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Absorbance/mAU
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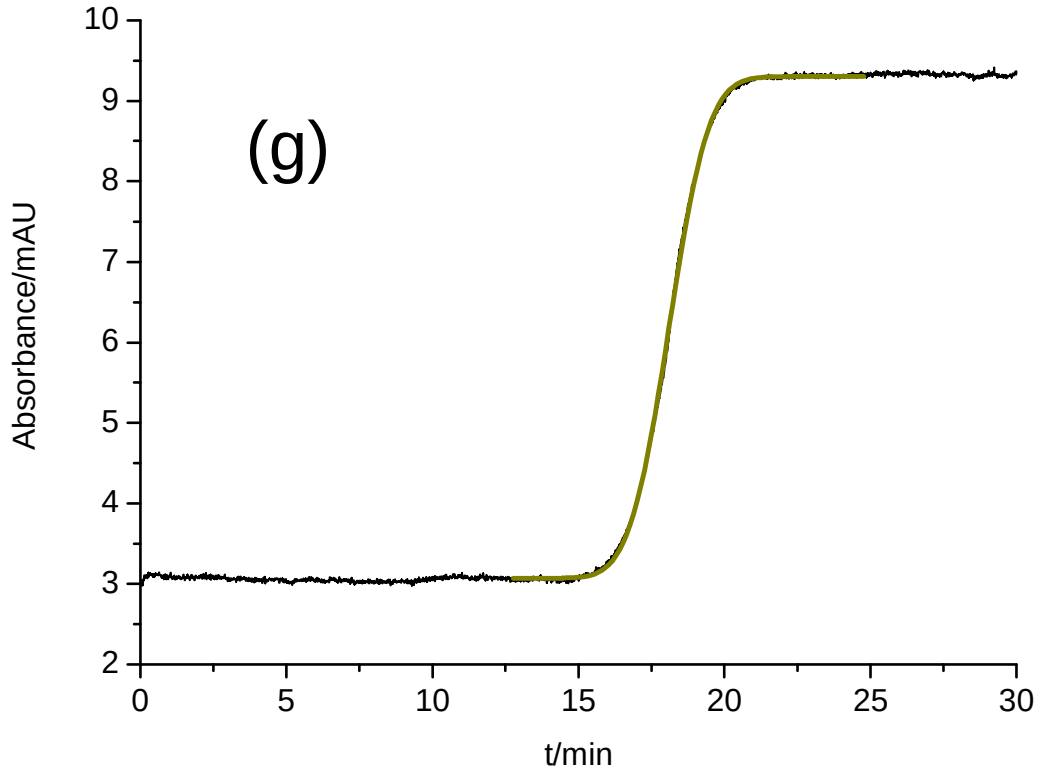

Figure S3. Recorded traces (TDA) for (a+b) SNP7, (c+d) SNP12, (e+f+g) SNP22. For experimental parameters refer to Table S2. Shown are different traces for the same sample, black = smoothed UV trace (FFT 10 points), green = fitted curve.

Table S1. Results of Taylor dispersion analysis, experimental conditions: T = 25 °C, total length of capillary = 606.5 mm, capillary length to detector = 505.5 mm, inner diameter of fused silica capillary = 76 μm, frontal method, pressure difference = 0.2 psi = 13.8 mbar, particle suspension diluted with 5 mmol L^{-1} borax in water against 5 mmol L^{-1} borax in water, mass fraction of nanoparticles in sample: 0.4% (SNP22) and 0.9 % (SNP12 and SNP7), absorbance detection at 200 nm.

Sample	Run	t_H/min	SE(t_H)/min	σ_t/min	SE(σ_t)/min	R^2	r_H/nm (1)	r_H/nm (2)
SNP7	1	18.19	0.00118	0.6774	0.00164	0.99776	6.173	6.171
	2	18.30	0.000954	0.6774	0.00133	0.99853	6.134	6.132
	3	18.43	0.000947	0.7029	0.00132	0.99860	6.560	6.559
	4	18.31	0.000918	0.6834	0.00128	0.99865	6.242	6.240
	5	18.32	0.00104	0.6912	0.00145	0.99828	6.381	6.380
	MW	18.31		0.6865			6.298	6.296
	SD	0.0845		0.0108			0.174	0.174
	RSD	0.46%		1.57%			2.77%	2.77%
SNP12	1	17.90	0.000930	0.7561	0.00127	0.99890	7.813	7.812
	2	18.01	0.000648	0.7165	0.000895	0.99940	6.975	6.973
	3	17.87	0.00102	0.7312	0.00135	0.99858	7.323	7.321
	4	17.88	0.000714	0.7417	0.000981	0.99931	7.528	7.527
	5	17.85	0.000784	0.7375	0.00107	0.99918	7.456	7.455
	MW	17.90		0.7366			7.419	7.418
	SD	0.0639		0.0144			0.306	0.306
	RSD	0.36%		1.97%			4.13%	4.13%
SNP22	1	17.65	0.000543	1.0357	0.000736	0.99974	14.87	14.87
	2	17.90	0.000630	1.05403	0.000851	0.99966	15.18	15.18
	3	18.34	0.000589	1.10218	0.000793	0.99971	16.21	16.21
	4	17.62	0.000503	1.07638	0.000683	0.99978	16.09	16.08
	5	18.10	0.000539	1.0713	0.000731	0.99975	15.51	15.51
	MW	17.92		1.0679			15.57	15.57
	SD	0.305		0.0249			0.572	0.572
	RSD	1.70%		2.34%			3.67%	3.67%

(1) Calculation via Taylor equation (*cf.*, Section S2); (2) calculation via Taylor-Aris equation (*cf.*, Section S2); MW = arithmetic mean; SD = standard deviation; RSD = relative standard deviation; R = correlation coefficient; SE = standard error resulting from regression analysis, r_H = hydrodynamic radius