Supporting Information

Restricted and Unrestricted Migration Mechanisms of Silica Nanoparticles in Agarose Gels and Their Utilization for the Separation of Binary Mixtures

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To determine the electrophoretic mobility and convert it correctly to the ζ-potential $\mathrm{K}a$ needs to be calculated. With this value the right correction factor f(Κa) can be chosen for the calculation of the ζ-potential. Table S1 shows the thickness of the electric double layer (Κ^{-1}) and the corresponding Κa-values depending on the TBE buffer concentration and its ionic strength, which is estimated by the measured conductivity and the following assumption:

$$\sigma = 150\,\frac{\mu S}{cm} \quad \triangleq \quad I = 1\,mmol$$

Next, the Κ-values were calculated by

$$\mathrm{K} = \frac{1}{0.304}\sqrt{I}\,nm^{-1},$$

which is valid for a monovalent electrolyte at a temperature of 25°C.[1]

(1) Israelachvili, J. N. *Intermolecular and Surface Forces*, 3th ed.; Elsevier, Academic Press: Amsterdam, 2011.

Table S1: Calculation of "Κa" to determine the right correction factor "f(Κa)"

particle size [nm]	TBE buffer conc.	measured conductivity [µS/cm]	ionic strength [mmol/L]	Κ [nm^{-1}]	Κ^{-1} [nm]	Κa [-]
50	0.00xTBE	3	0.02	0.02	63.85	0.78
	0.25xTBE	298	1.99	0.15	6.82	7.33
		496	3.31	0.19	5.29	9.46

	0.50xTBE					
	1.00xTBE	771	5.14	0.24	4.24	11.79
	2.00xTBE	1123	7.49	0.28	3.51	14.23
	5.00xTBE	1205	8.03	0.29	3.39	14.74
	10.00xTBE	1334	8.89	0.31	3.22	15.51
100	0.50xTBE	496	3.31	0.19	5.29	18.92
300	0.50xTBE	496	3.31	0.19	5.29	56.75

For the extraction of NP from the agarose gel the “pool method” was used. Figure S2 (top) depicts schematically the procedure to obtain the NP in the TBE buffer as a suspension, whereas Figure S2 (bottom) presents photographs indicating a particle migration (white band) from the gel into the buffer.

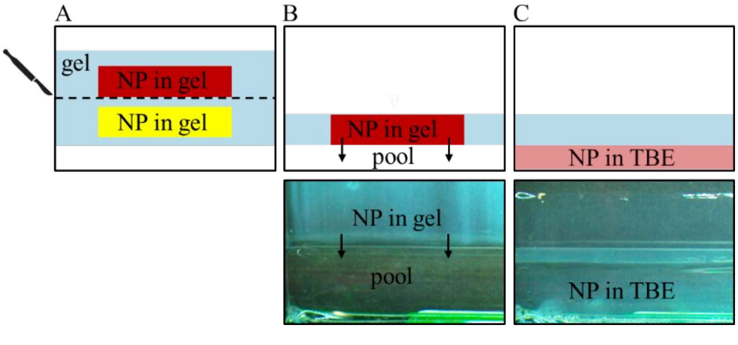


Figure S2: Schematic depiction of the “pool method” for extraction of particles from a gel fragment after the electrophoretic experiment (top) and corresponding photographs (bottom)

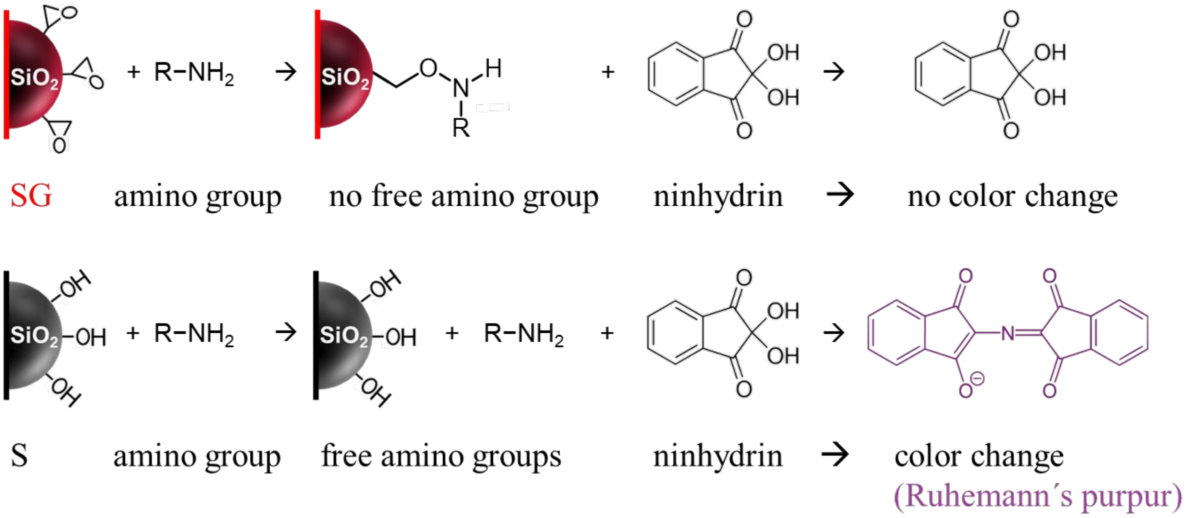


Figure S3: Schematic reaction path of the ninhydrin test with unmodified as well as GLYMO-modified SiO_2 NP whereby the Ruhemann´s purple is formed under the presence of free amino groups

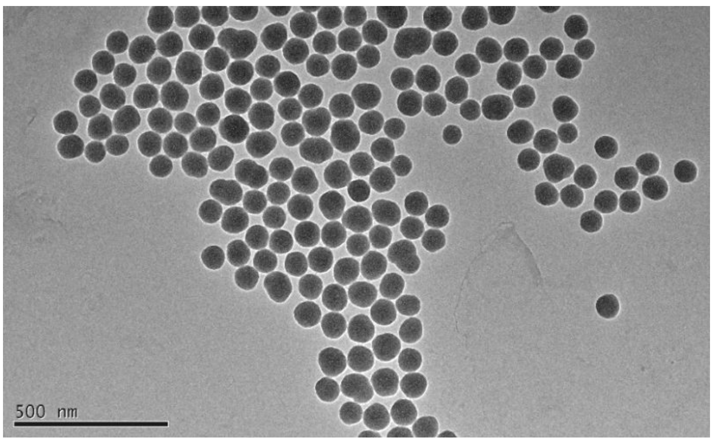


Figure S4: Exemplary TEM image of spherical SiO_2 nanoparticles of sample B ($x_{50,3}$ = 91 nm)

Table S5: Measured free-solution electrophoretic mobilities of the SiO_2 samples A-D and their corresponding Smoluchowski ζ-potentials as well as their “Κα” values

Electrophoretic mobility [μmcm/V*s]

sample	at 60 V	at 80 V	at 100 V
A	-2.11	-2.14	-2.20
B	-2.40	-2.56	-2.64
C	-2.56	-2.75	-2.80
D	-3.03	-3.22	-3.28

Zeta potentials [mV]

sample	at 60 V	at 80 V	at 100 V		Κa [-]
A	-31.5	-31.9	-32.8		10.78
B	-35.8	-38.1	-39.3		17.59
C	-38.2	-41.0	-41.8		26.67
D	-45.2	-48.0	-48.9		55.99

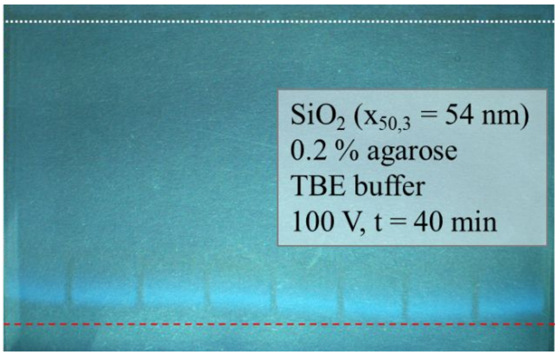
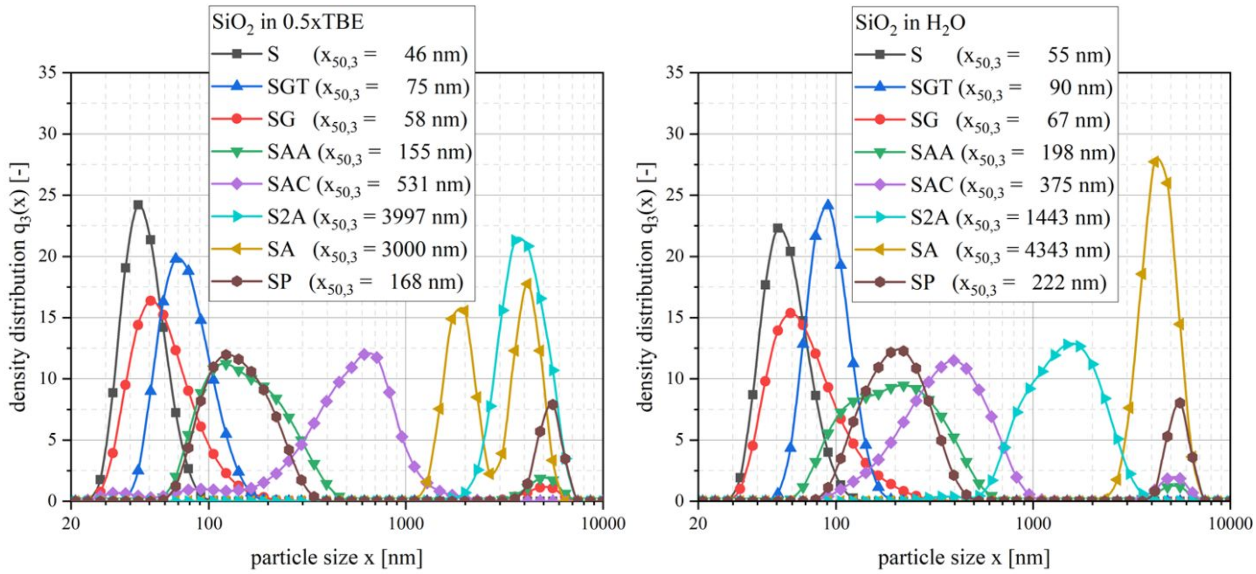


Figure S6: Photograph of SiO_2 NP ($x_{50,3}$ = 54 nm) in a 0.2 wt.-% agarose gel after migration for 40 min at an applied voltage of 100 V. All pockets were filled with the same sample so that the smiling effect is visible



	in H_2O	in 0.5 TBE buffer solution			
sample	size [nm]	size [nm]	μE [μmcm/Vs]	ζ at 100 V [mV]	Ka [-]
S	55	46	-2.9	-43	10
SGT	90	75	-2.3	-34	17
SG	67	58	-1.9	-29	13
SAA	198	155	-1.8	-26	37
SAC	375	531	-1.5	-23	71
S2A	1443	3997	-0.1	-2	273
SA	4343	3000	0.6	9	822
SP	222	168	1.4	21	42

Figure S7: PSD in H_2O as well as 0.5xTBE buffer solution, measured free-solution electrophoretic mobilities, Smoluchowski ζ-potentials and "Κα" values *of modified SiO_2 NP*

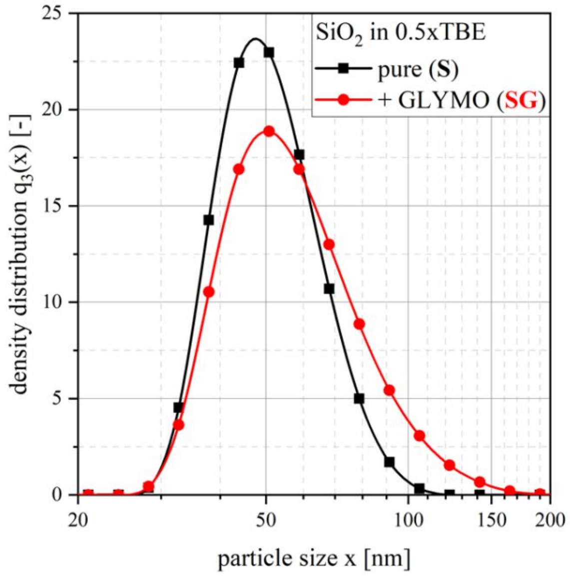


Figure S8: PSD of unmodified (S) and GLYMO-modified SiO_2 NP (SG) for the unrestricted separation