

## Stable dispersions of ferromagnetic carbon-coated metal nanoparticles: preparation *via* surface initiated atom transfer radical polymerization (SI-ATRP)

### Supporting information:

Supporting Information 1:

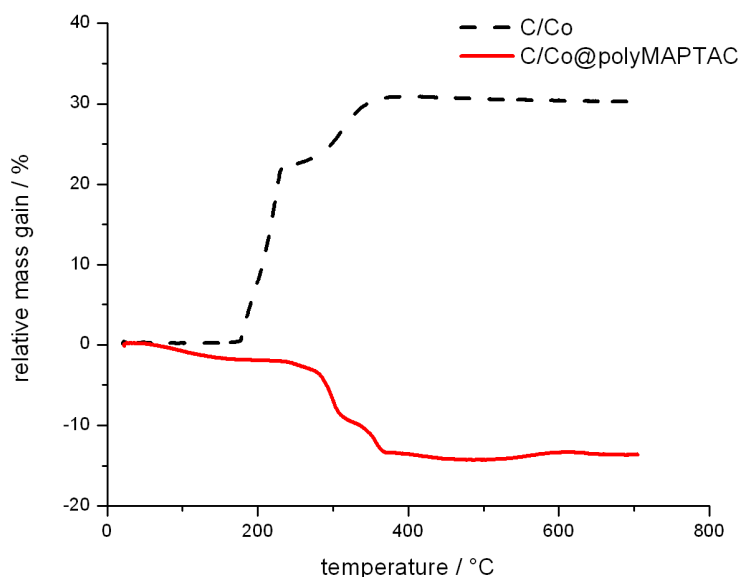
Physisorption of polydiallyldimethylammonium chloride [1]:

500 mg particles were dispersed in water by ultrasonication. 250 mg polydiallyldimethylammonium chloride (PADMAC) solution (200'000- 350'000 20% solution in water, Aldrich) was added and stirred over night. Particles were washed with water, ethanol and acetone by magnetic decantation procedure.

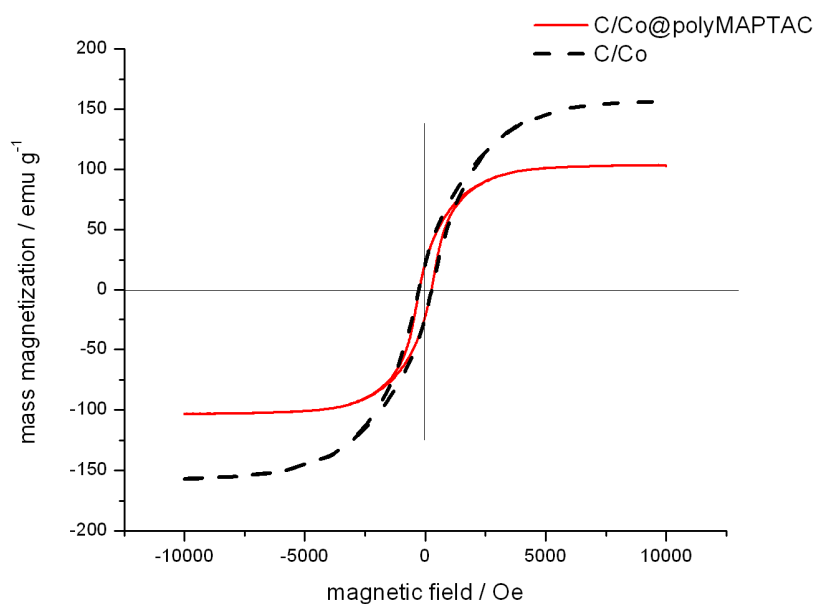
Supporting Table 1

Product	C (wt%)	N (wt%)	Cl (wt%)
C/Co with physisorbed PADMAC	4.2	0.01	0.04

**Supporting Figure S1:** microanalysis of physisorbed polydiallyldimethylammonium chloride on C/Co.

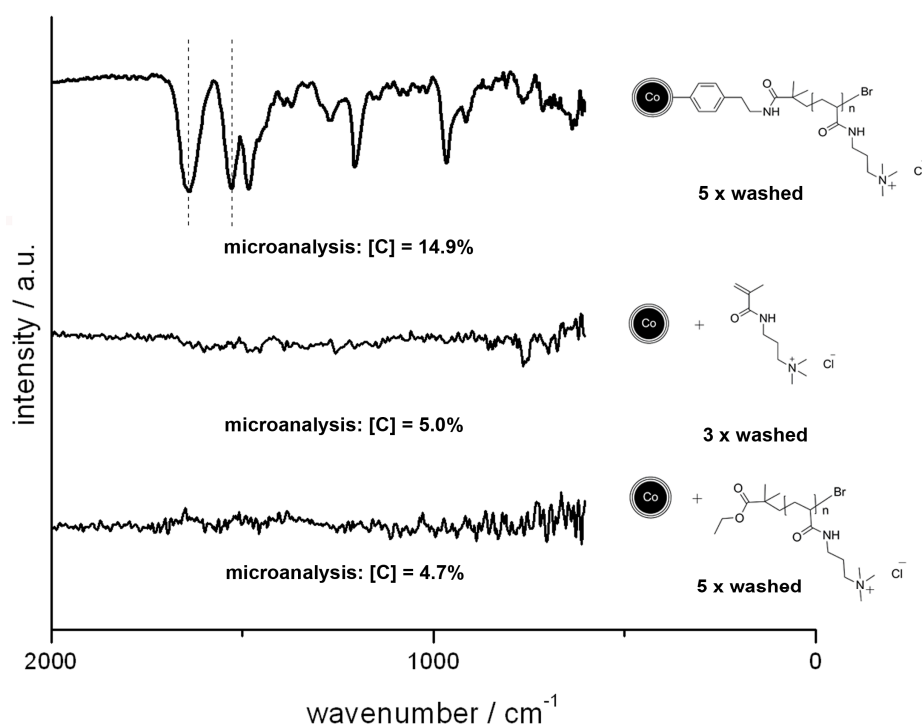


**Supporting Figure S2:** thermogravimetric measurements of C/Co 1 (dashed) and C/Co@polyMAPTAC 7 (solid). When the graphene-like carbon of the pristine C/Co particles combusts, a mass gain is detectable as the elemental cobalt oxidizes.

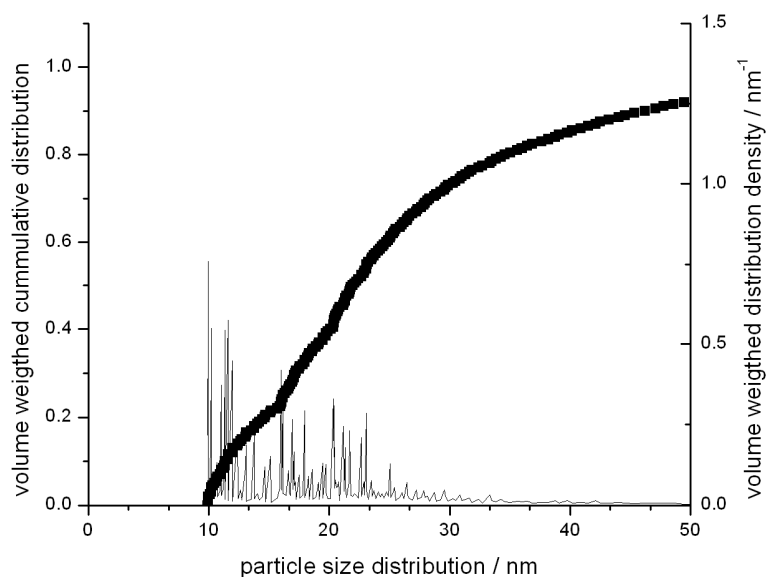


**Supporting Figure S3:** Magnetic hysteresis susceptibility (VSM) of C/Co **1** (dashed) and C/Co@polyMAPTAC **7** (solid).

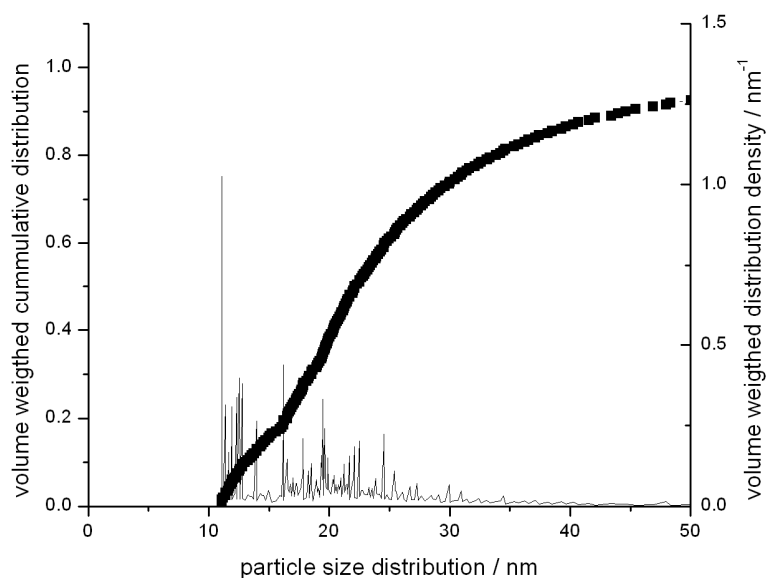
According to calculations out of the thermogravimetric analysis, C/Co@polyMAPTAC nanoparticles **7** should exhibit 60% of mass magnetization compared to pristine C/Co **1**. Comparison of the measured VSM values provide a mass magnetization of 65 % for modified **7** compared to non-functionalized particles **1**.



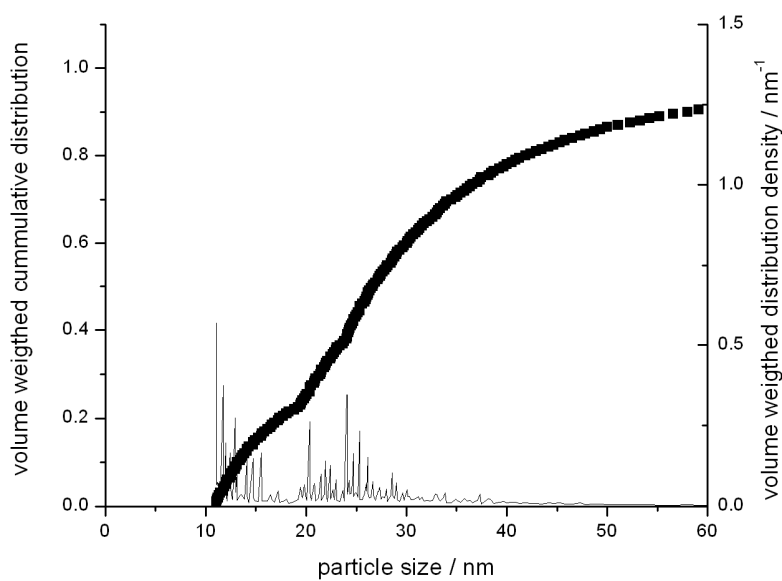
**Supporting Figure S4:** Infrared spectra and microanalysis (C content in wt%).  
C/Co@polyMAPTAC (top), C/Co after mixing with MAPTAC monomer under  
reaction condition (middle) and C/Co after polymerization of MAPTAC in presence  
of unbound initiator (bottom).



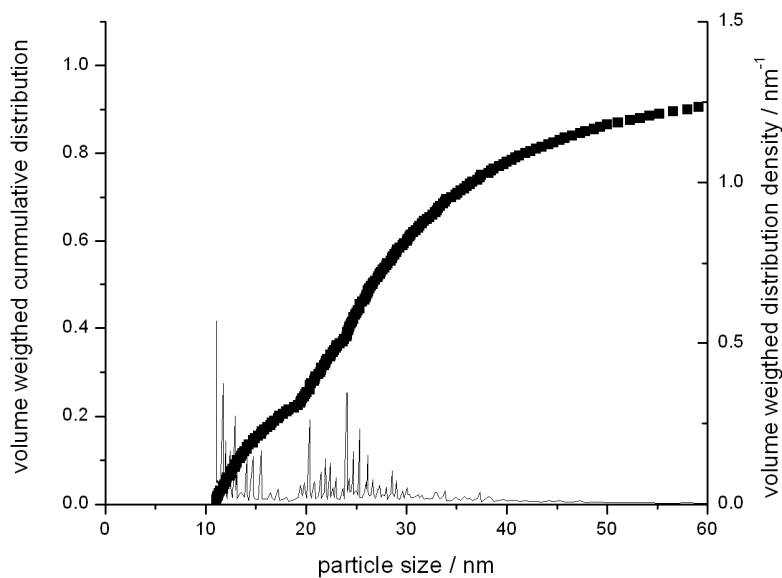
**Supporting Figure S5:** Particle size distribution of C/Co@polyMAPTAC in 10mM  
NaCl Solution measured by LumiSizer.



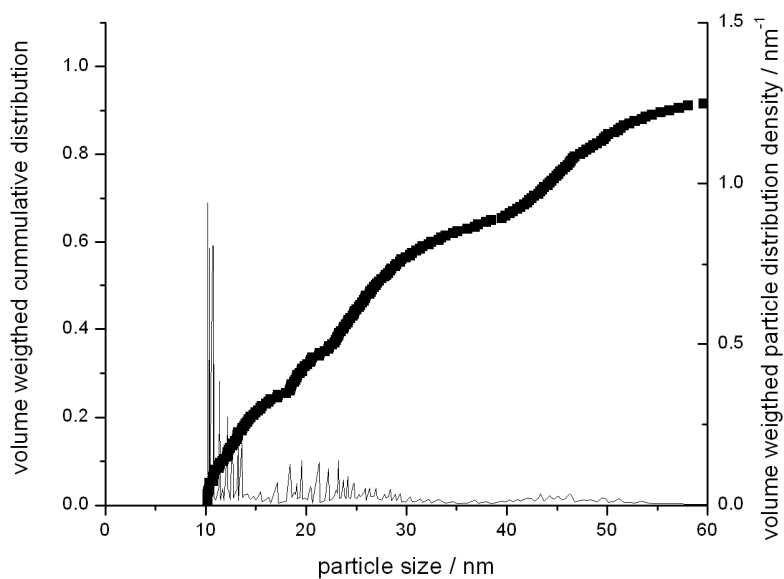
**Supporting Figure S6:** Particle size distribution of C/Co@polyMAPTAC in 1M  
NaCl Solution measured by LumiSizer.



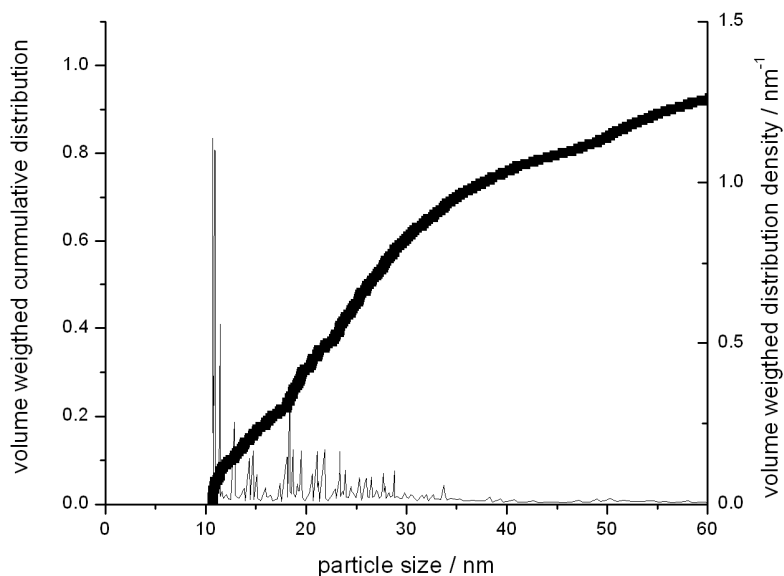
**Supporting Figure S7:** Particle size distribution of C/Co@polyMAPTAC in 1M CaCl<sub>2</sub> Solution measured by LumiSizer.



**Supporting Figure S8:** Particle size distribution of C/Co@polyMAPTAC in 0.33M CaCl<sub>2</sub> Solution measured by LumiSizer.



**Supporting Figure S9:** Particle size distribution of C/Co@polyMAPTAC in 10mM  $\text{CaCl}_2$  Solution measured by LumiSizer.



**Supporting Figure S10:** Particle size distribution of C/Co@polyMAPTAC in 0.33mM  $\text{CaCl}_2$  Solution measured by LumiSizer.

### **DLVO Theory presumptions and calculations:**

Total interaction potential of 2 identical spheres in a medium consists of 4 additive potentials:

$$V_{total}(d) = V_{vdW}(d) + V_{el.-stat}(d) + V_{magn}(d) + V_{steric}(d)$$

*Attractive Interactions:*

Van der Waals Potential  $V_{vdW}(d)$

Magnetic Attraction  $V_{magn}(d)$

*Repulsive Interactions:*

Steric repulsion  $V_{steric}(d)$

Electrostatic repulsion  $V_{el.-stat}(d)$

$$V_{vdW}(d) = -\frac{R}{12d}(\sqrt{A_m} - \sqrt{A_p})^2 \quad [2,3]$$

$$V_{magn}(d) = -\frac{8\pi}{72} \frac{\mu_0 M^2 D^3}{(2d/D + 2)^3} \quad [2,4]$$

$$V_{steric}(d) = \begin{cases} 2\pi kTR^2 \xi \left[ 2 - \frac{l+2}{t} \ln\left(\frac{1+t}{1+l/2}\right) - \frac{l}{t} \right] & \text{for } r/2s \leq 1 \\ 0 & \text{for } r/2s \geq 1 \end{cases}$$

$$V_{el.-stat}(d) = -9.22 \cdot 10^{-11} \tanh^2\left(\frac{\psi}{103}\right) \frac{R}{2} \exp(\kappa d)$$

$$l = d/R$$

$$t = s/R$$

$d$	distance between particles (from the surface)	x-axis
$R = 15 \cdot 10^{-9} m$	average particle radius from TEM images	
$D = 30 \cdot 10^{-9} m$	average particle diameter from TEM images	
$A_m = 3.7 \cdot 10^{-20}$	Hamaker-constant of the medium (water)	[3]
$A_p = 30 \cdot 10^{-20}$	Hamaker-constant of the particles (Cobalt)	[3]
$\mu_0 = 4\pi \cdot 10^{-7} Vs / Am$	Vacuum permeability	
$M_s = 917000 A/m$	Saturation magnetization from VSM measurements	
$M_R = 198000 A/m$	Remanence from VSM measurements	
$kT \approx 4.1 \cdot 10^{-21} J$	thermal energy at room temperature	
$s = 6.2 \cdot 10^{-9} m$	shell thickness of the polymer shell calculated from microanalysis	
$\xi = 2.6 \cdot 10^{18} m^{-2}$	surface concentration of adsorbed molecules	[3]
$1/\kappa$	Debye length	[3]

$$\kappa = 1.04 \cdot 10^9 \text{ m}^{-1}$$
$$\psi = 50 \text{ mV} \quad \text{surface potential} \quad [3]$$

$$M_s = 340 \text{ memu} / 3.3 \text{ mg} = 103 \text{ emu} / \text{g} = 917 \text{ emu} / \text{cm}^3 = 917000 \text{ A} / \text{m}$$

$$M_R = 73.3 \text{ memu} / 3.3 \text{ mg} = 22.2 \text{ emu} / \text{g} = 198 \text{ emu} / \text{cm}^3 = 198000 \text{ A} / \text{m}$$

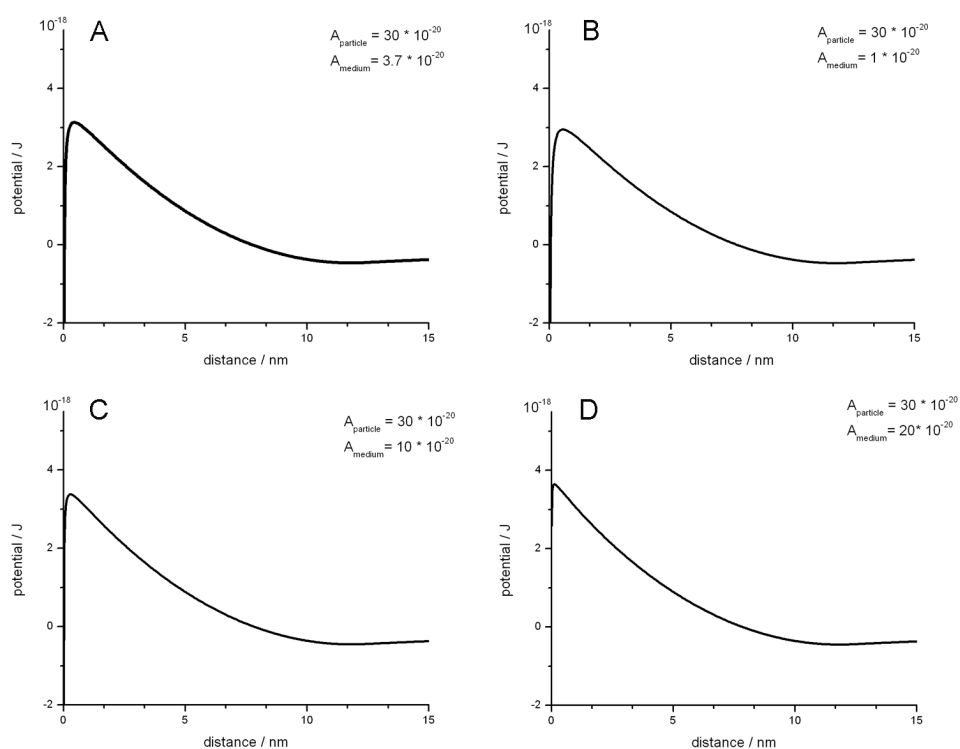
$$1/\kappa = ((0.304 \cdot 10^{-9}) / \sqrt{M_{\text{electrolyte}}}) \text{ m for 1:1 electrolytes (e.g., NaCl, 0.1 mol/l)}$$

$$\rho_{Co} = 8.9 \text{ g} / \text{cm}^3$$

Some assumptions were made on the basis of literature-known values. There are three parameters which were suggested like this (Hamaker constant, surface potential, electrolyte concentration).

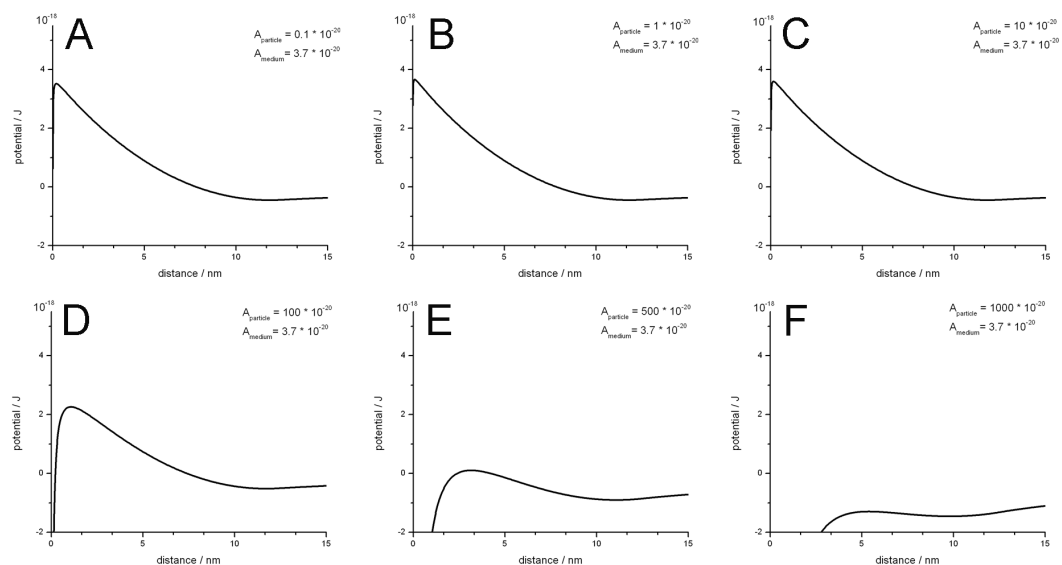
The impact of these parameters was proven by simulation of the total potential with variation of these values.

There are two different Hamaker constants ( $A_p$  = constant of the particle,  $A_m$  = constant of the medium surrounding the particles).



**Supporting Figure S11:** Variation of the Hamaker-constant of the medium (A:  $A_m = 3.7 \times 10^{-20}$ , B:  $A_m = 1 \times 10^{-20}$ , C:  $A_m = 10 \times 10^{-20}$ , D:  $A_m = 20 \times 10^{-20}$ )

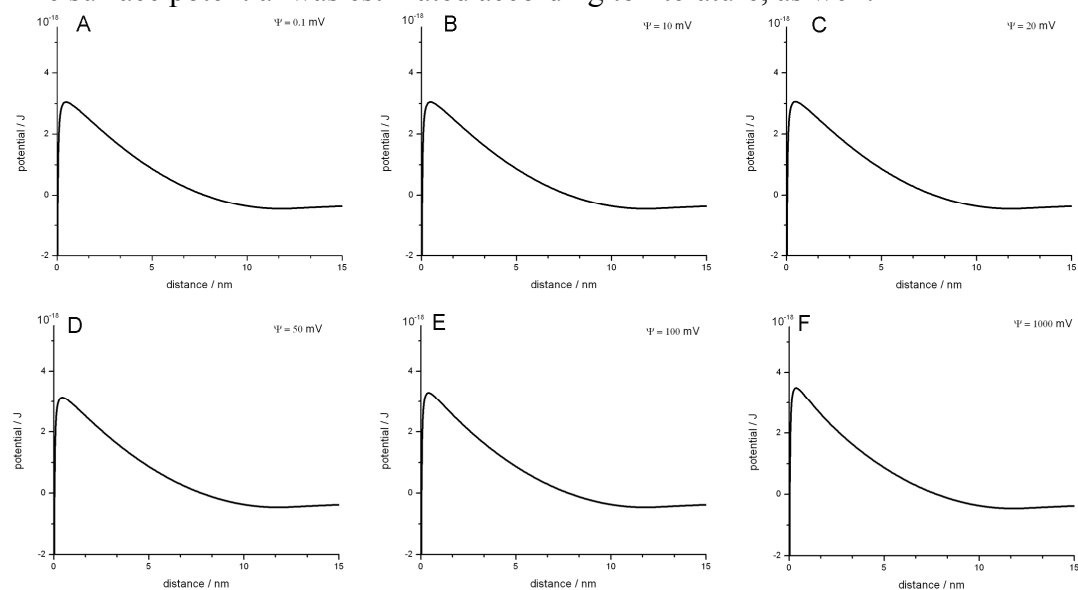
Variation of the Hamaker-constant of medium leads to only slight change of the total potential. Therefore, the influence of this Hamaker-constant can be suggested as negligible.



**Supporting Figure S12:** Variation of the Hamaker-constant of the particle (**A:**  $A_p = 0.1 \cdot 10^{-20}$ , **B:**  $A_p = 1 \cdot 10^{-20}$ , **C:**  $A_p = 10 \cdot 10^{-20}$ , **D:**  $A_p = 100 \cdot 10^{-20}$ , **E:**  $A_p = 500 \cdot 10^{-20}$ , **F:**  $A_p = 1000 \cdot 10^{-20}$ )

According to literature, the values of Hamaker-constants for a metallic particle lie between  $10$  and  $50 \cdot 10^{-20}$  [3]. From the simulated potentials it is obvious, that an influence of this constant on the total potential only takes place from  $100 \cdot 10^{-20}$  and higher.

The surface potential was estimated according to literature, as well.

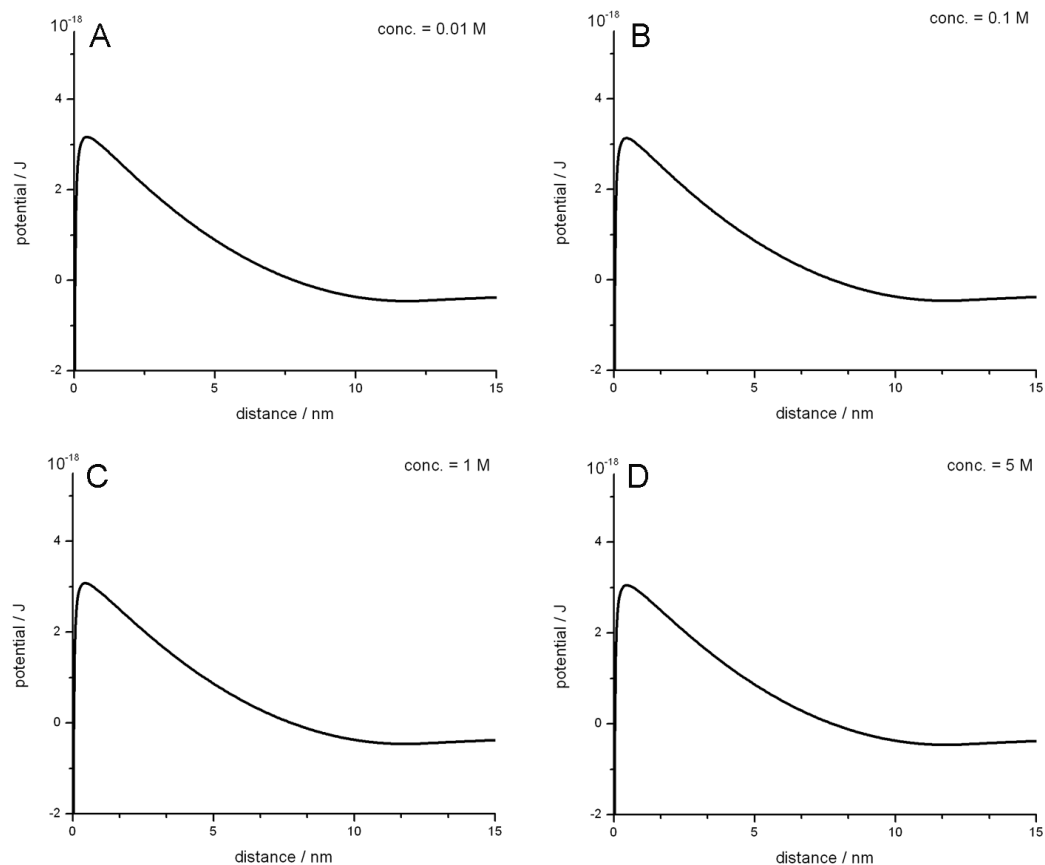


**Supporting Figure S13:** Variation of the surface potential  $\Psi$  (**A:**  $\Psi = 0.1$  mV, **B:**  $\Psi = 10$  mV, **C:**  $\Psi = 20$  mV, **D:**  $\Psi = 50$  mV, **E:**  $\Psi = 100$  mV, **F:**  $\Psi = 1000$  mV).

As there is no big change of the total potential by variation of the surface potential, our estimation can be accepted without further doubt.

The last parameter includes the salt concentration, which affect the Debye-length and is connected with the  $\kappa$ .





**Supporting Figure S14:** Variation of the molarity of the medium (**A:** conc.= 0.01 M, **B:** conc.= 0.1 M, **C:** conc.= 1 M, **D:** conc. = 5 M)

The molarity of the solution has a sparse impact on the total potential as well. Theoretically, there is no significant change by variation of the electrolyte concentration.

With regard on the variation of these parameters and their influence, the chosen variables seem to be reliable.

#### References:

- [1] M. Rossier, F. M. Koehler, E. K. Athanassiou, R. N. Grass, B. Aeschlimann, D. Guenther and W. J. Stark, *Journal of Materials Chemistry*, 2009, **19**, 8239-8243.
- [2] Rodriguez, Stability and magnetorheological behavior of magnetic fluids based on ionic liquids, 2011 **J. Phys.: Condens. Matter** 23
- [3] Israelachvili, Intermolecular and Surface forces
- [4] Rosensweig, Ferrohydrodynamics