

SUPPORTING INFORMATION

Surface Charging and Interfacial Water Structure of Amphoteric Colloidal Particles

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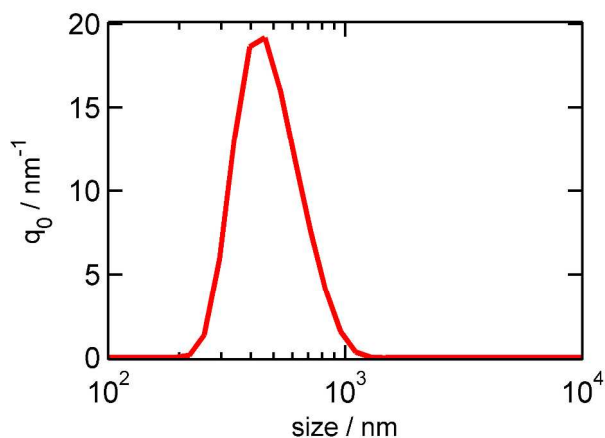
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Characterization of particle size

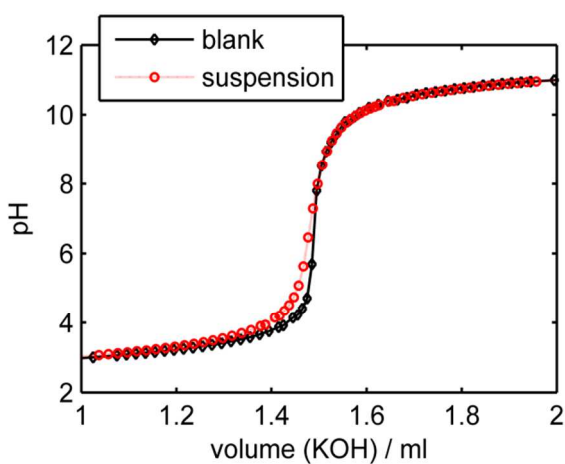
The shape of second-harmonic scattering profiles from colloidal suspensions depends, amongst others on the particle size.^{1,2} The size distribution of the particles used in our study (micromere® 01-01-502, micromod Partikeltechnologie, Germany) was characterized by dynamic light scattering (DLS). For the DLS measurements a concentration of 50 µg/ml was adjusted and a Malvern Instruments (UK) Zetasizer nano ZS was used. The result is shown in Figure S1



S1. Particle size distribution of the amino- and sulfate terminated polystyrene particles. The mean radius measured by dynamic light scattering is 258 ± 3 nm

Potentiometric titration

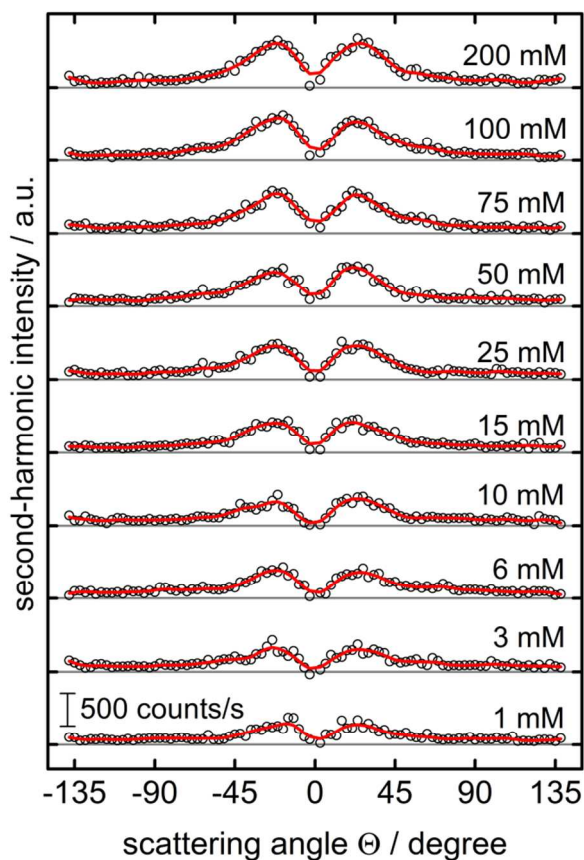
Potentiometric titrations were conducted in as reported in the main paper. Representative titration curves for a blank experiment and for the titration of a particle suspension are shown in Figure S2. A cubic spline was used to interpolate pH values between the measurement points. From the volume difference of the blank and solutions with particles the amount of proton adsorption was calculated.



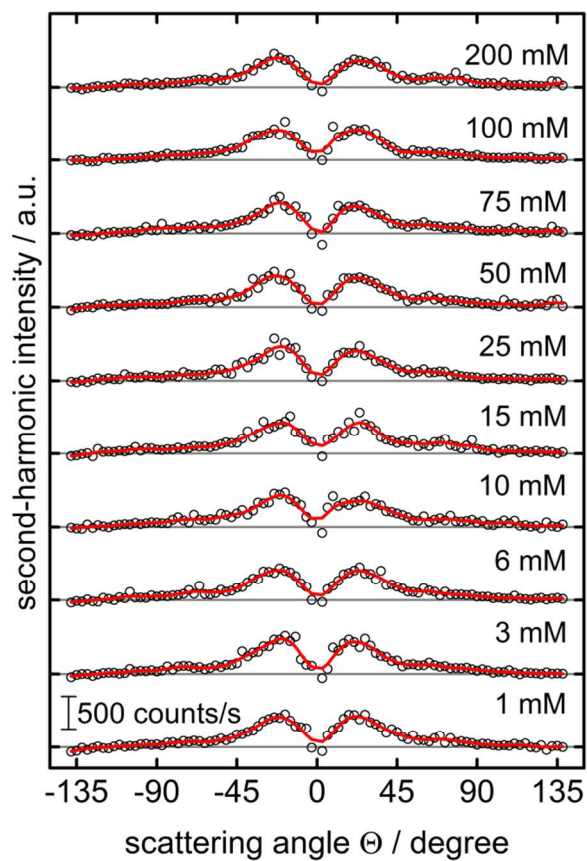
S2. Potentiometric titrations of amphoteric polystyrene particles by KOH. Excess HCl was added to adjust an initial pH of approximately 2.5.

Charge screening experiments

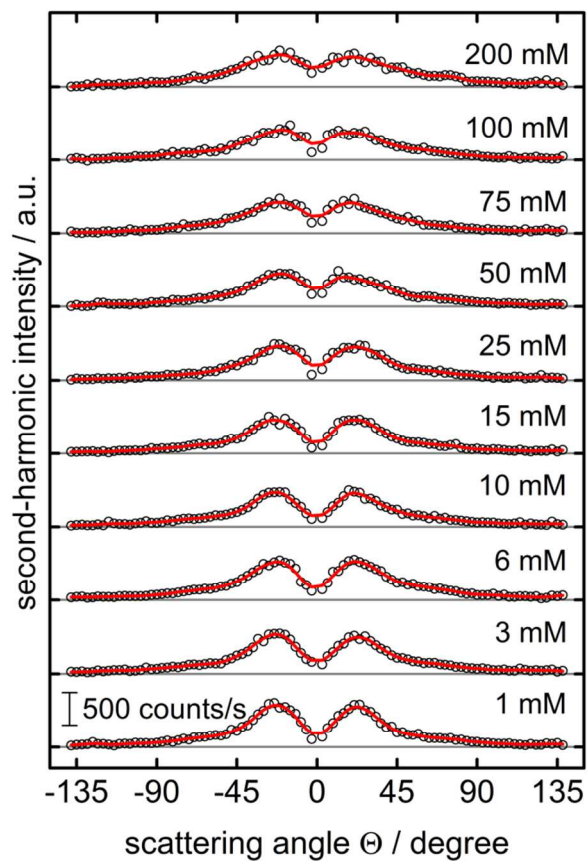
Second-harmonic scattering profiles of the charge screening experiments at pH values of 3, 5.1 and 8.4 are presented in figures S3 – S4. Experiments were conducted in as described in the main paper.



S3. Second-harmonic scattering profiles (SH intensity vs. scattering angle Θ) of the amphoteric polystyrene particles as a function of ionic strength at pH 3. $\Theta = 0^\circ$ is the propagation direction of the fundamental light. Light grey lines indicate zero intensity and the red lines are a guide to the eye.



S4. Second-harmonic scattering profiles (SH intensity vs. scattering angle Θ) of the amphoteric polystyrene particles as a function of ionic strength at pH 5.2. $\Theta = 0^\circ$ is the propagation direction of the fundamental light. Light grey lines indicate zero intensity and the red lines are a guide to the eye.



S5. Second-harmonic scattering profiles (SH intensity vs. scattering angle Θ) of the amphoteric polystyrene particles as a function of ionic strength at pH 8.4. $\Theta = 0^\circ$ is the propagation direction of the fundamental light. Light grey lines indicate zero intensity and the red lines are a guide to the eye.

Derivation

The probability that water molecules are aligned with their dipole moments parallel to the interfacial electric field is:

$$\langle p \rangle = N \cdot \langle p_z \rangle = N \frac{\int_0^{r'} \int_0^{2\pi} \int_0^\pi p \cdot \cos \vartheta \cdot \exp\left(\frac{-pE^{dc} \cos \vartheta}{k_B T}\right) \cdot r \sin \vartheta d\varphi d\vartheta dr}{\int_0^{r'} \int_0^{2\pi} \int_0^\pi \exp\left(\frac{-pE^{dc} \cos \vartheta}{k_B T}\right) \cdot r \sin \vartheta d\varphi d\vartheta dr} =$$

which can be simplified to:

$$= N \frac{\int_0^\pi p \cdot \cos \vartheta \cdot \exp\left(\frac{-pE^{dc} \cos \vartheta}{k_B T}\right) \sin \vartheta d\vartheta}{\int_0^\pi \exp\left(\frac{-pE^{dc} \cos \vartheta}{k_B T}\right) \sin \vartheta d\vartheta}$$

N is the number density of interfacial molecules, ϑ is the angle of the molecular dipole with respect to the direction of the electric field E^{dc} , p is the molecular dipole moment, T is the temperature and k_B the Boltzmann constant. By substituting $x = \cos \vartheta$ and $dx = -\sin \vartheta d\vartheta$ we get:

$$\langle p \rangle = N \frac{\int_1^{-1} p \cdot x \cdot \exp\left(\frac{-pE^{dc} x}{k_B T}\right) dx}{\int_1^{-1} \exp\left(\frac{-pE^{dc} x}{k_B T}\right) dx}$$

With

- $g(x) = px$
- $f'(x) = \exp\left(\frac{-pE^{dc} x}{k_B T}\right)$
- $\int_a^b g(x) f'(x) dx = [g(x) f(x)]_a^b - \int_a^b f(x) g'(x) dx$

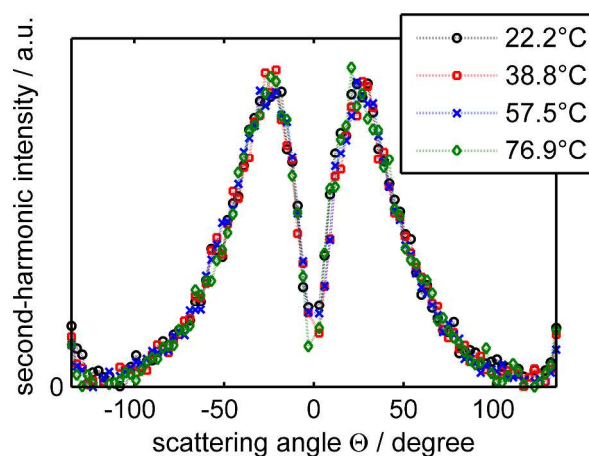
we get:

$$\langle p \rangle = N \cdot p \frac{\left[-\frac{k_B T}{pE^{dc}} \cdot \exp\left(\frac{-pE^{dc} x}{k_B T}\right) x \right]_1^{-1} - \left[\left(\frac{k_B T}{pE^{dc}}\right)^2 \cdot \exp\left(\frac{-pE^{dc} x}{k_B T}\right) \right]_1^{-1}}{\left[\frac{k_B T}{pE^{dc}} \cdot \exp\left(\frac{-pE^{dc} x}{k_B T}\right) \right]_1^{-1}} =$$

$$\begin{aligned}
&= N \cdot p \frac{\left(\exp\left(\frac{pE^{dc}}{k_B T}\right) + \exp\left(\frac{-pE^{dc}}{k_B T}\right) \right) - \left(\frac{k_B T}{pE^{dc}}\right) \left(\exp\left(\frac{pE^{dc}}{k_B T}\right) - \exp\left(\frac{-pE^{dc}}{k_B T}\right) \right)}{\left(\exp\left(\frac{pE^{dc}}{k_B T}\right) - \exp\left(\frac{-pE^{dc}}{k_B T}\right) \right)} = \\
&= N \cdot p \frac{\cosh\left(\frac{p \cdot E^{dc}}{k_B \cdot T}\right) - p \left(\frac{k_B \cdot T}{p \cdot E^{dc}}\right) \cdot \sinh\left(\frac{p \cdot E^{dc}}{k_B \cdot T}\right)}{\sinh\left(\frac{p \cdot E^{dc}}{k_B \cdot T}\right)} = N \cdot p \left[\coth\left(\frac{p \cdot E^{dc}}{k_B \cdot T}\right) - \left(\frac{k_B \cdot T}{p \cdot E^{dc}}\right) \right]
\end{aligned}$$

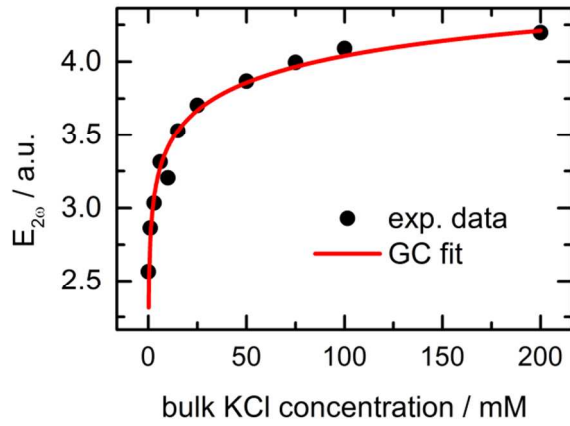
Temperature effect

Second-harmonic scattering profiles at a pH of 10.1 and different temperatures are presented in Figures S6. As described in the main paper, at a pH of around 10 the particles have a maximum overall surface charge of 26 mC/m². If the charge dependent contribution to the total SH field is dominated by an alignment of water molecules, the SH intensity should decrease when the temperature of the suspension is increased. A close inspection of Figure S6 reveals, that within the accuracy of our measurement the SH intensity remains constant as temperature is increased. This supports our assumption, that a realignment of water molecules plays a minor role in our experiments. Details are discussed in the main paper.



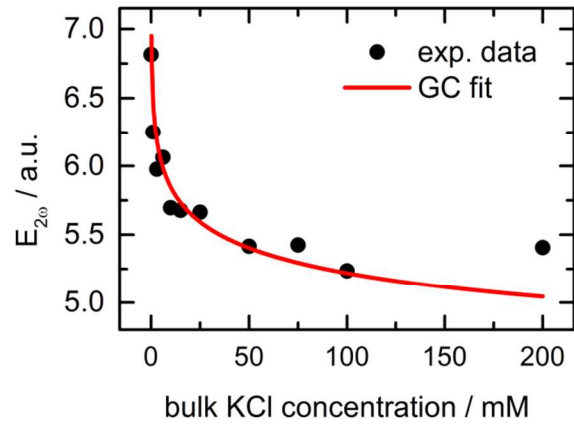
S6. Second-harmonic scattering profiles (SH intensity vs. scattering angle Θ) of the amphoteric polystyrene particles as a function of temperature. $\Theta = 0^\circ$ is the propagation direction of the fundamental light.

Analysis of the charge screening experiments with constant B and charge densities obtained from potentiometric titrations



Fit parameter for pH = 3.0

$$A = 4.9; B = -11.00; \sigma = 0.0224 \text{ C/m}^2$$



Fit parameter for pH = 8.4

$$A = 4.3; B = 11.00; \sigma = -0.0256 \text{ C/m}^2$$

S7. Evaluation of charge screening data with constant B and charge densities obtained from potentiometric titrations.

Figure S7 shows, that it is possible to reproduce our experimental findings with a constant value for B and charge densities obtained by titration experiments. However, we find in this second analysis, that A at pH 3.0 (4.9) exceeds A at pH 8.4 (4.3). This is inconsistent with the asymmetry we find in the pH dependent SHG data (compare Figure 4a, main manuscript).

Determination of NH₂ density by SPDP method

SPDP (N-succinimidyl 3-(2-pyridyldithio) propionate) is a crosslinker for proteins comprising primary amines and / or sulfhydryls³. Here the reagent is used to determine the surface density of amino groups, where in a first step SPDP was covalently bonded to surface amino groups and the particles were washed thoroughly to remove excess SPDP. In a second step, pyridine-2-thione is displaced by the reducing agent dithiothreitol (DDT). The concentration of displaced pyridine-2-thione can be determined by measuring the absorbance at 343 nm and corresponds to the amount of amino surface groups. The method was applied according to the instructions of the manufacturer of the kit (Thermo Scientific Pierce Protein Biology Products). The molar absorptivity of pyridine-2-thione is $8.080 \cdot 10^3 \text{ M}^{-1} \text{cm}^{-1}$.³ The results are summarized in Table 1.

Table 1. Determination of NH₂ density by SPDP method

| $\Delta A_{343\text{nm}} / -$ | $c_{\text{particle}} / (\text{g/l})$ | $c_s(\text{NH}_2) / (\mu\text{mol/g})$ | $c_s(\text{NH}_2) / \text{nm}^{-2}$ |
|-------------------------------|--------------------------------------|--|-------------------------------------|
| 0.52035 ± 0.0025 | 12.38 | 5.20 ± 0.03 | 0.28 ± 0.002 |

REFERENCES

- (1) Wunderlich, S.; Schürer, B.; Sauerbeck, C.; Peukert, W.; Peschel, U. Molecular Mie Model for Second Harmonic Generation and Sum Frequency Generation. *Phys. Rev. B* **2011**, *84*, 235403-1 - 235403-9.
- (2) Jen, S. H.; Dai, H.-L.; Gonella, G. The Effect of Particle Size in Second Harmonic Generation from the Surface of Spherical Colloidal Particles. II: The Nonlinear Rayleigh-Gans-Debye Model. *J. Phys. Chem. C* **2010**, *114*, 4302–4308.
- (3) Carlsson, J.; Drevin, H.; Axen, R. Protein Thiolation and Reversible Protein-protein Conjugation. N-Succinimidyl 3-(2-pyridyldithio). *Biochem. J.* **1978**, *173*, 723–737.