Supplementary Material of

Particle adsorption at the oil-water interface studied with second harmonic generation

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Section Ⅰ: Characterization of the polystyrene particles

A. Analysis certificate of the latex beads

Analysis certificates provided by the manufacturer (Life Technologies, Invitrogen, Thermo Fisher Scientific) show that the surface charge groups of the latex beads with sulfate, amidine, and carboxyl functional groups are 440, 300 and 59, respectively, measured by the charge titration method.

B. Characterization of the zeta potentials and size distribution

Table S1 The size and zeta potential of latex beads measured by dynamic light scattering (Malvern Instruments Ltd., Zetasizer Nano ZS90, UK).

	Size (nm)	**Zeta Potential (mV)**
Sulfate latex	18.4 ± 1.5	-59.6 ± 2.4
Amidine latex	24.5 ± 1.1	72.8 ± 1.7
Carboxyl latex	28.9 ± 1.2	-42.3 ± 0.9

C. Measurements of the pH and ionic strength

The measured pH and the estimated ionic strength of aqueous solution with latex beads at different concentrations used in this work were shown in Table S2. The ionic strength was estimated based on the conductivity as a function of NaCl concentration shown in Table S3, S4 and S5. It can be seen that the measured ionic strength for all three kinds of latex beads is at the level comparable to NaCl solution in the range of 10^{-5} M to 10^{-4} M.

Table S2 pH of the aqueous solution with latex beads at different concentrations used in this work.

	Concentration	**pH**
Sulfate latex	0.1 nM	5.5 ± 0.1
	56 nM	5.0 ± 0.1
Amidine latex	0.05 nM	7.0 ± 0.1

	23 nM	6.6 ± 0.1
Carboxyl latex	0.2 nM	6.6 ± 0.1
	67 nM	6.1 ± 0.1

Table S3 Conductivity (from the dynamic light scattering experiment) of the aqueous solution with sulfate latex beads at different NaCl concentrations.

NaCl	**Conductivity (mS/cm)**	
concentration	**Sulfate latex 0.1 nM**	**Sulfate latex 56 nM**
0 M	0.067	0.42
1×10^{-6} M	0.067	0.43
1×10^{-5} M	0.083	0.47
1×10^{-4} M	0.50	0.85
1×10^{-3} M	4.02	4.43
1×10^{-2} M	39.31	39.94

Table S4 Conductivity (from the dynamic light scattering experiment) of the aqueous solution with amidine latex beads at different NaCl concentrations. "—" indicates a failed measurement possibly due to low particle concentration.

NaCl	**Conductivity (mS/cm)**	
concentration	**Amidine latex 0.05 nM**	**Amidine latex 23 nM**
0 M	—	0.083
1×10^{-6} M	—	0.083
1×10^{-5} M	0.10	0.13
1×10^{-4} M	0.48	0.48
1×10^{-3} M	3.95	3.98
1×10^{-2} M	38.89	37.04

Table S5 Conductivity (from the dynamic light scattering experiment) of the aqueous solution with carboxyl latex beads at different NaCl concentrations.

NaCl concentration	Conductivity (mS/cm)	
	Carboxyl latex 0.2 nM	Carboxyl latex 67 nM
0 M	0.083	0.47
1×10^{-6} M	0.050	0.43
1×10^{-5} M	0.10	0.47
1×10^{-4} M	0.48	0.87
1×10^{-3} M	4.20	4.48
1×10^{-2} M	38.46	40.24

Section Ⅱ: SHG response and zeta potential from the hexadecane/water interface as a function of CTAB surfactant concentration

Figure S1 shows the SHG intensity and zeta potential from the hexadecane/water interface as a function of CTAB surfactant concentration replotted based on the data from our previous work [1]. Clearly, there was a remaining SHG emission (~50±10 % in intensity) from the oil-water interface with the interface at nearly zero potential. That is, $I_{SHG} \propto |\chi^{(2)}|^2 \approx 50\% \left|\chi^{(2)} + \chi^{(3)}\Phi(0)\cos(\varphi_{DC})e^{i\varphi_{DC}}\right|^2$. So, we have the approximate relation as: $\left|\chi^{(2)} + \chi^{(3)}\Phi(0)\cos(\varphi_{DC})e^{i\varphi_{DC}}\right| \approx 1.4\chi^{(2)}$.

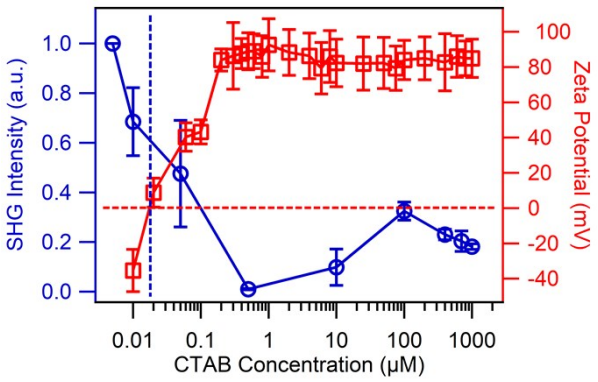

Figure S1 SHG intensity and zeta potential from the hexadecane/water interface as a function of CTAB surfactant concentration.

References

1. W. Wu, H. Fang, F. Yang, S. Chen, X. Zhu, Q. Yuan and W. Gan, *J. Phys. Chem. C*, 2016, **120**, 6515-6523.