Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary material

for

Reversible Assembly of Silica Nanoparticles at Water-Hydrocarbons Interfaces Controlled by SDS Surfactant

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S1. The hydroxylation reaction of silica nanoparticles

The hydroxylation reaction between non bridging oxygens on 3 nm silica nanoparticles and hydrogen atom in the water phase are probed using reactive forcefield molecular dynamics simulations implemented in the Amsterdam density functional (ADF) software. The silica nanoparticle dissolved in 1 g/cm^3 of water are initially inserted in a simulation box of 5 nm × 5 nm × 5 nm dimensions in x, y, and z directions. NVT simulations are carried out on the optimized initial configuration for 250 ps under 298 K. Silica nanoparticles and water molecules are modeled using the forcefield developed by Fogarty and co-workers.[1] The temperature was controlled by Nose-Hoover thermostat with a constant of 1 fs. The snapshot shown in **Figure S1** are taken from different frames in the trajectory file to show the progress in the hydroxylation reactions occur on the surface of the silica nanoparticle. The number of water molecules and the total energy of the system as a function of the simulation time are shown in **Figure S2**.

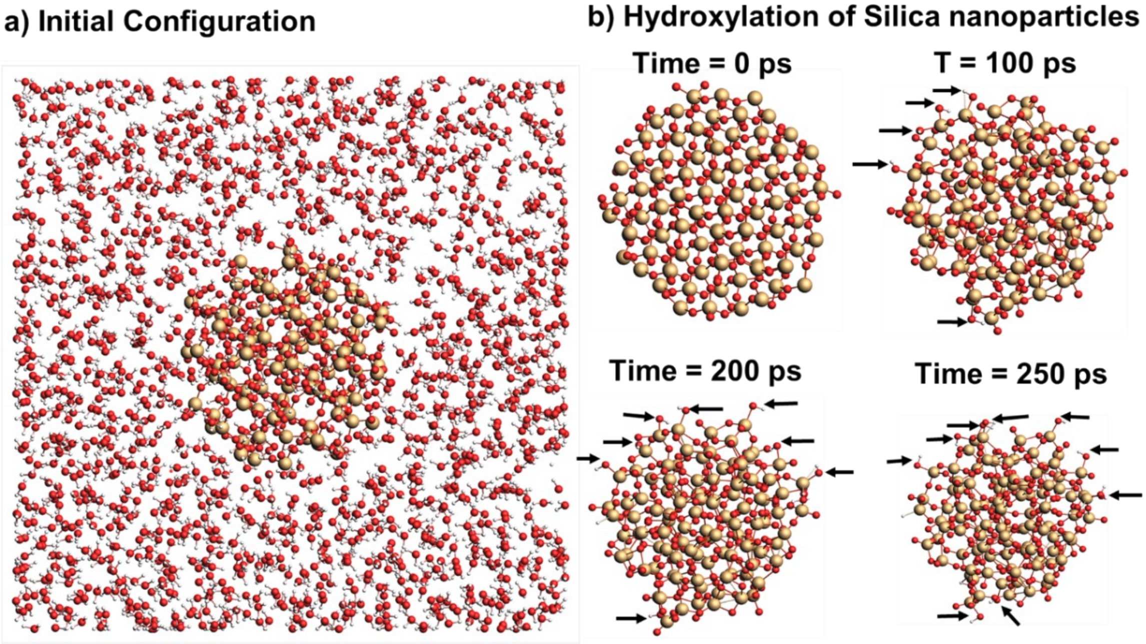


Figure S1. Snapshots of the (a) initial configuration and (b) the progress of the hydroxylation reaction of the nonbridging oxygens with water molecules. The snapshots are taken from ReaxFF simulations of silica nanoparticles dissolved in water at 298 K and 1 bar.

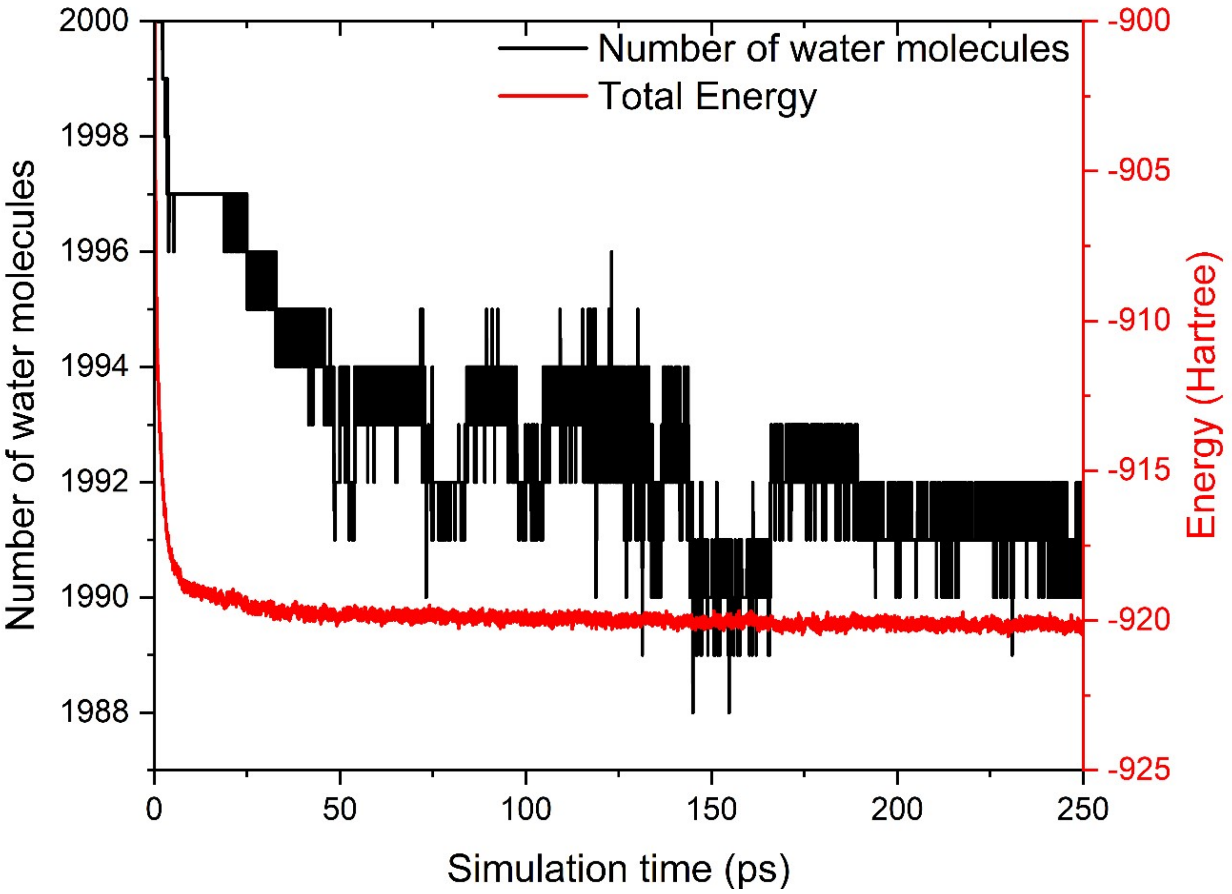
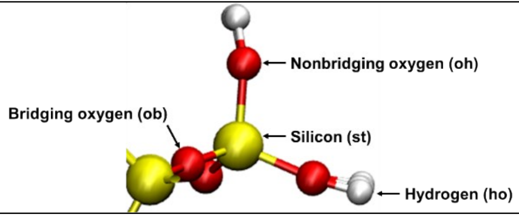
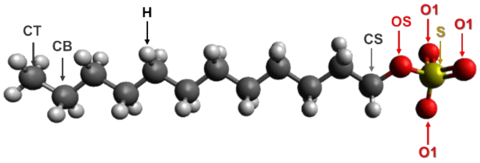


Figure S2. The profiles of water molecules and the total energy of the simulated silica nanoparticle in water as a function of the simulation time. The reduction in the number of water molecules is solely due to the hydroxylation reaction of the nonbridging oxygens on the surface of the silica nanoparticle.

Forcefield Parameters

The forcefields parameters of SDS surfactant and silica nanoparticles are depicted in **Table 2**. The snapshots are labeled to show the molecule name and the corresponding parameters. The snapshot from silica nanoparticles are taken for a silanol group (SiOH) on the surface of the nanoparticle and the associated bridging oxygens.

Table S1. The forcefields parameters of the atoms in silica nanoparticles and SDS surfactant taken from the references listed in Ref. column. The appended snapshots explains the atomic description of the nanoparticles and the surfactant.

Atom	σ (nm)	ε (kJ/mol)	q (e)	Ref.
Parameters for Silica				
Si	0.302	7.7006×10^{-6}	2.1000	[2]
O bridging	0.316	0.650190	-1.0500	[2]
O nonbridging	0.316	0.650190	-0.9500	[2]
H	0.000	0.000000	0.4250	[2]
Parameter for SDS				
S	0.355	1.0460	1.284	[3, 4]
O1	0.315	0.8368	-0.654	[3, 4]
OS	0.296	0.7111	-0.459	[3, 4]
CS	0.350	0.2761	0.017	[3, 4]
CB	0.350	0.2761	-0.120	[3, 4]
CT	0.350	0.2761	-0.180	[3, 4]
H	0.250	0.1255	0.060	[3, 4]

σ is the finite distance at which the interatomic potential is zero.

ε is the depth of the potential well.

q is the atomic charge.

The scattering of the bulk nanoparticles

USAXS/SAXS measurements are taken from the nanoparticles in the bulk phase of water are shown in **Figure S3**. The power law slope of < 1 in the Q regions < 10^{-3} indicates that the nanoparticles are well dispersed, unlike the interfacial nanoparticles that assemble at water-heptane and water-toluene interfaces in the absence of SDS surfactant. The size distribution of the dispersed nanoparticles in the 50 nm and 100 nm solutions are 51.35 ± 3.15 nm and 101.35 ± 4.17 nm, respectively.

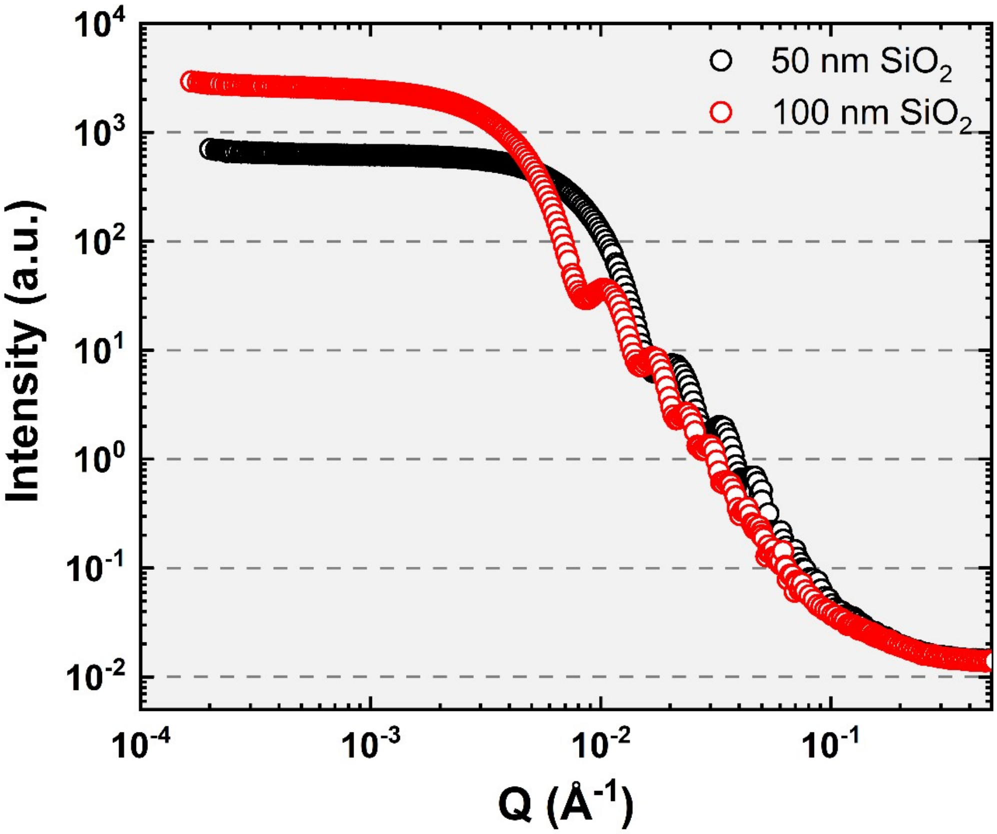


Figure S3. Small angle X-ray scattering from the silica nanoparticles with diameters of 50 nm and 100 nm dispersed in the bulk water.

Hydrogen bonding interactions

The hydrogen bonds profiles of nanoparticles-water and SDS-water are shown in **Figure S4 and S5**. Hydrogen bonds between nanoparticles and water increase as the SDS concentration increase due to the displacement of the nanoparticles into the aqueous phase. Similarly, hydrogen bonds between the hydrophilic head in the SDS molecule and the interfacial water increases with the SDS concentration due to the increase in SDS molecules at the interfaces.

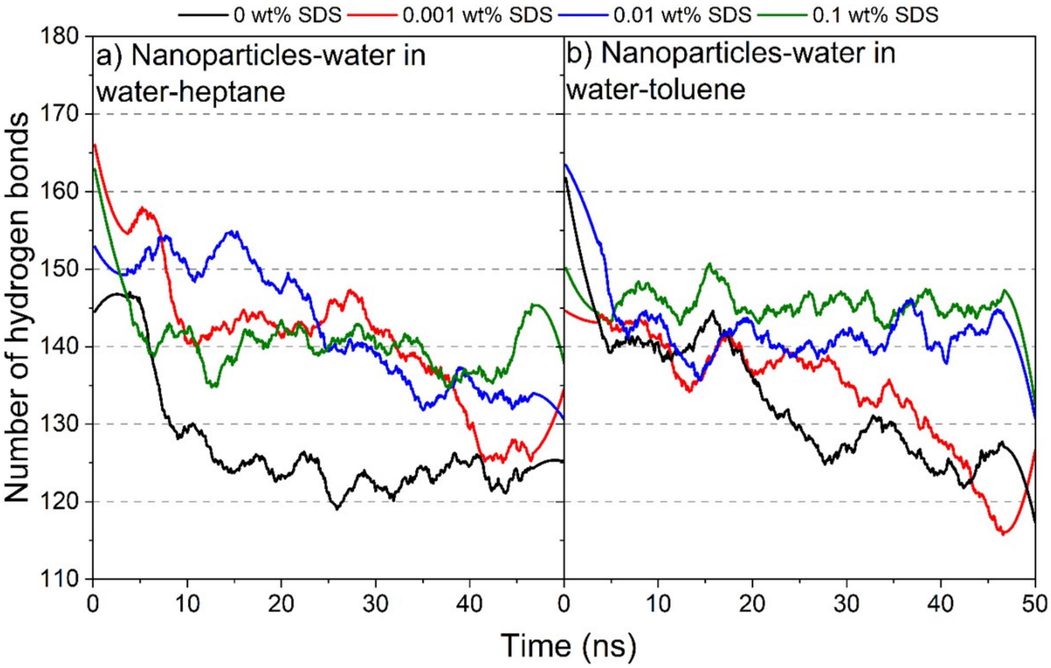


Figure S4. Hydrogen bonding profiles of silica nanoparticles and water molecules in water-heptane and water-toluene emulsions as a function of the SDS concentration and the simulation time.

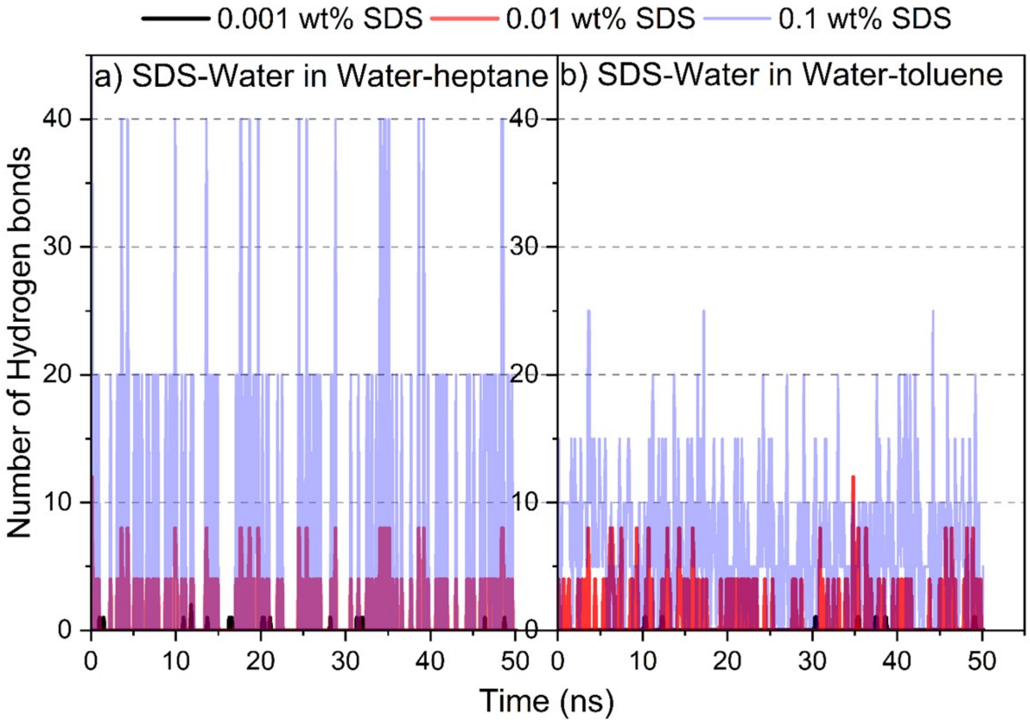


Figure S5. Hydrogen bonding profiles of SDS surfactant and water molecules at water-heptane and water-toluene interfaces as a function of the SDS concentration and the simulation time.

References

1. J.C. Fogarty, H.M. A.Y. Aktulga, Grama, A.C. Van Duin and S.A. Pandit, *J. Chem. Phys.*, 2010, **132**, 174704.
2. R.T. Cygan, J.J. Liang, A.G. Kalinichev, *J. Phys. Chem. B*, 2004, **108**, 1255-1266.
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