Supplemental Information for:

Creating Nanoparticle Stability in Ionic Liquid $[C_4mim][BF_4]$ by Inducing Solvation Layering

Jingsi Gao,[†] Rose S. Ndong,[† #] Mark B. Shiflett,[‡] and Norman J. Wagner[*†]*

†Center for Molecular and Engineering Thermodynamics, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States

‡Central Research and Development, DuPont Company, Wilmington, Delaware 19880, United States

#Current Address: Solvay USA Inc., 350 George Patterson Boulevard, Bristol, PA 19007, United States

Surface modification and characterization

Colloidal silica dioxide nanoparticles (NexSil 125-40) were purchased from Nyacol Nano Technologies, Inc and used as received (40 wt% solid in H_2O with sodium stabilizing counterion as supplied). The fluorocarbon 1H,1H,9H hexadecafluoro-1-nonanol (CAS 376-18-1, $C_9H_4F_{16}O$, from Matrix Scientific) was covalently grafted to the nanoparticle surface *via* an esterification reaction following the protocol of van Helden *et al*.[1] After the reaction, the modified nanoparticles were thoroughly washed 3 times with ethanol using a Sorvall RC6+ centrifuge. Finally, the particles were stored in ethanol until use and no visual sedimentation was observed, even after 4 months. The chemical grafting was confirmed by proton nuclear magnetic resonance (^{1}H NMR) using a Bruker AV-400 instrument. The grafting density of the fluorocarbon and the particle surface coverage were determined by thermogravimetric analysis (TGA, TA Instruments Q500) measurement.

Thermogravimetric Analysis

The grafting density of fluorocarbon onto particle surface is measured by thermogravimetric analysis (TGA) using a TA Instruments Q500 with flowing nitrogen gas condition. The temperature was increased from 25 °C to 80 °C in a rate of 10 °C/min and equilibrated at 80 °C for 20 min to remove physically adsorbed water. Then the temperature was increased to 900 °C in the same rate before and equilibrated at 900 °C for 15 min to ensure the complete decomposition of coated fluorocarbon. The TGA results as mass fraction versus temperature for uncoated and coated silica particles are shown in Figure S1. The uncoated particles show a weight loss of about 2.3 wt%, which is attributed to the desorption of physically adsorbed water. The coated particles have a weight loss of about 4.5 wt %, which indicates the additional presence of the surface modifier. From this weight loss, we calculated the graft density to be 1.4 chain/nm^2 of particles based on a particle average radius of 54.2 nm obtained by SANS. This value is lower than graft densities for octadecyl alcohol (2.9/nm^2) reported previously[2] and is about 28-35% of the estimated 4-5 surface silanol groups on amorphous silica.[3] This graft

density is consistent with the larger molecular size of the fluorinated compound. The calculated graft density corresponds to ~ 60 % of the theoretical maximum surface coverage, which is calculated using the molecular size calculated from the bond lengths, angles and atom sizes.

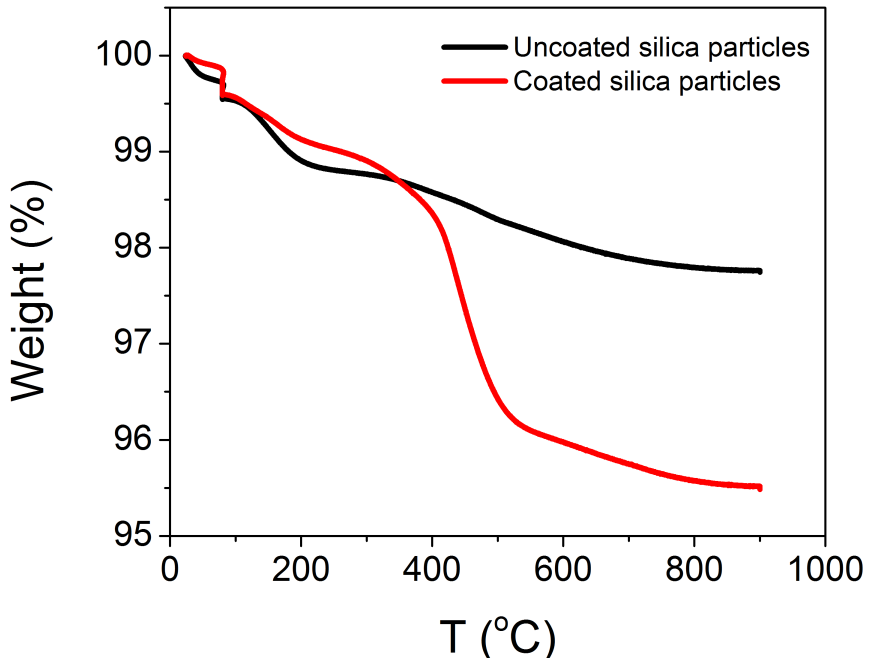

Figure S1. TGA curves for uncoated and coated particles, showing a weight loss of 2.3 wt% and 4.5 wt% for uncoated and coated particles, respectively.

Dynamic Light Scattering Measurement

The diffusivity of uncoated silica particles and coated silica particles suspension in various solvent were measured using a Brookhaven Instruments ZetaPals dynamic light scattering to determine the particle stability. Uncoated silica particles well dispersed in H_2O and fluorocarbon coated silica particles well dispersed in ethanol with a narrow size distribution. It's evident that uncoated silica particles aggregate in IL $[C_4mim][BF_4]$ with wide size distribution while coated particles stabilized in $[C_4mim][BF_4]$ with much narrow size distribution compared to the uncoated one. The values of the number average particle size reported from the instrument are reported in Table S1.

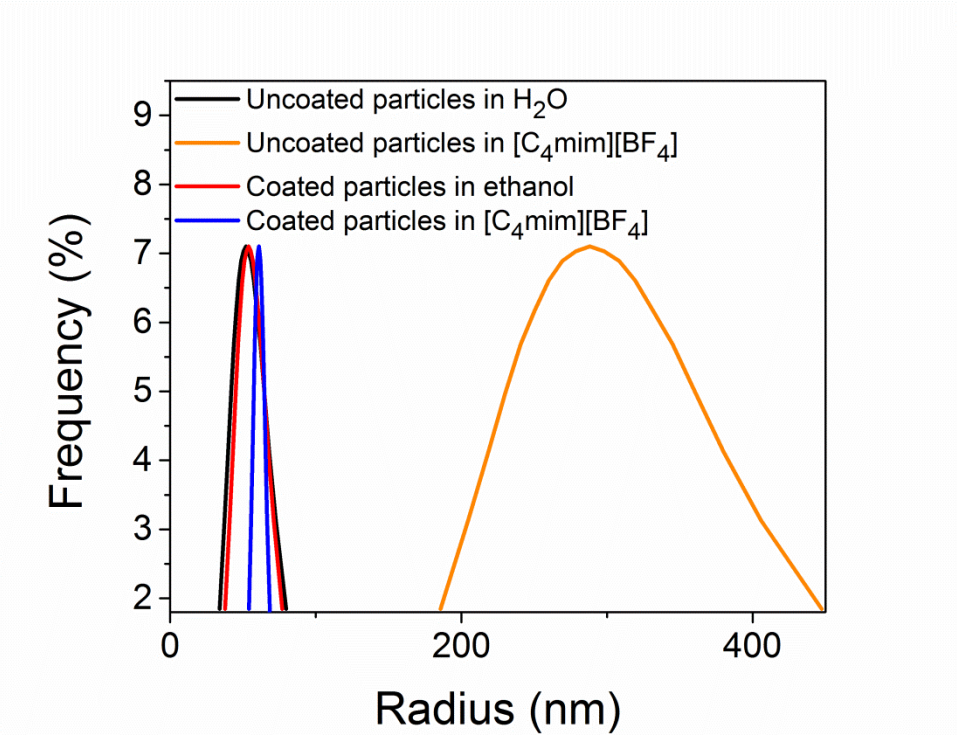

Figure S2. Size distribution of uncoated and coated particles suspended in various solvents from DLS measurement.

Table S1. Particle radii for uncoated and coated particles in various solvent measured by DLS.

Solutions	Uncoated particle in H_2O	Uncoated particle in $[C_4mim][BF_4]$	Coated particle in ethanol	Coated particle in $[C_4mim][BF_4]$
Radius (nm)	53.8 ± 4.8	298.6 ± 28.1	55.2 ± 3.8	60.4 ± 3.0

Silica Particle Density

Densitometry was performed on both the uncoated particles suspended in 0.1 mM NaCl/H_2O (pH = 9.1 ± 0.1) solution, and the coated particles suspended in $[C_4mim][BF_4]$ at 25 °C using an Anton Paar DMA-4500M densitometer. The experimental results can be seen in Figure S3. The skeletal particle density in solution is extracted from a linear regression of equation 1 to the data and found to be ϱ = 2.210 ± 0.005 g/cm^3 and ϱ = 2.167 ± 0.007 g/cm^3 for the uncoated and coated particles, respectively. The reduction in solution density of the coated particles is attributed to the contribution from the surface layer, where the fluorocarbon coating is expected to have a lower density than the silica nanoparticle.

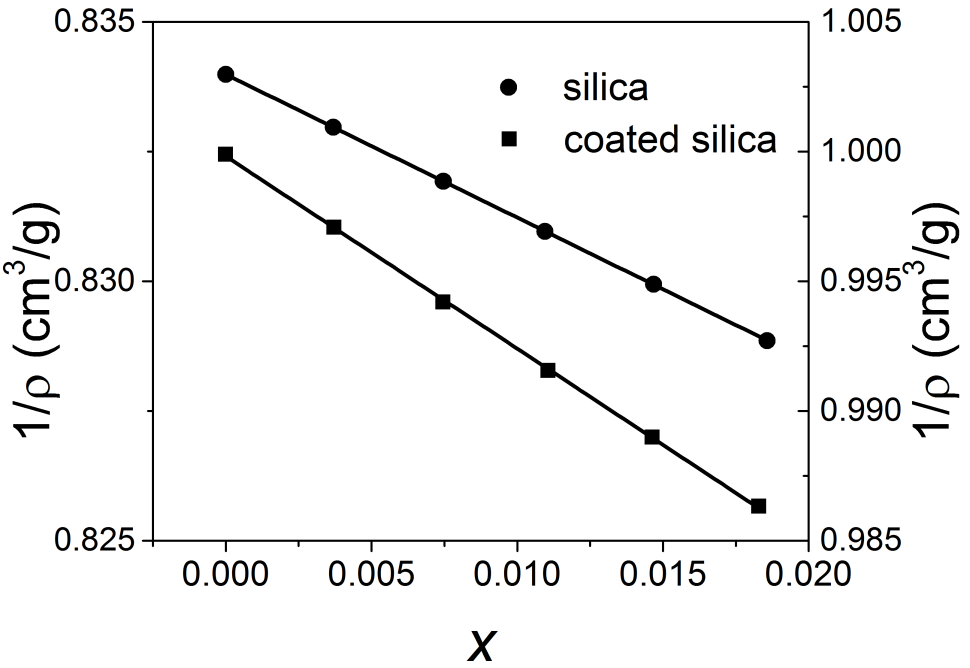

Figure S3. Results of the densitometry experiments for the uncoated silica particles in mother liquid (secondary y axis, right) and fluorocarbon coated silica particles in $[C_4mim][BF_4]$ (primary y axis, left). The lines represent a fit of equation 1 (in the Method section) to the inverse of the suspension density and the mass fraction of the disperse phase.

Proton Nuclear Magnetic Resonance (^{1}H NMR)

The ^{1}H NMR of uncoated silica particle, fluorocarbon coated silica particle and fluorocarbon suspended in deuterated chloroform ($CDCl_3$) are shown in Figure S4. The fluorocarbon coated silica particle shown the same chemical shift peaks profile as fluorocarbon at 4.1 ppm and 5.9-6.2 ppm indicating successful coating of fluorocarbon on to the particle surface.

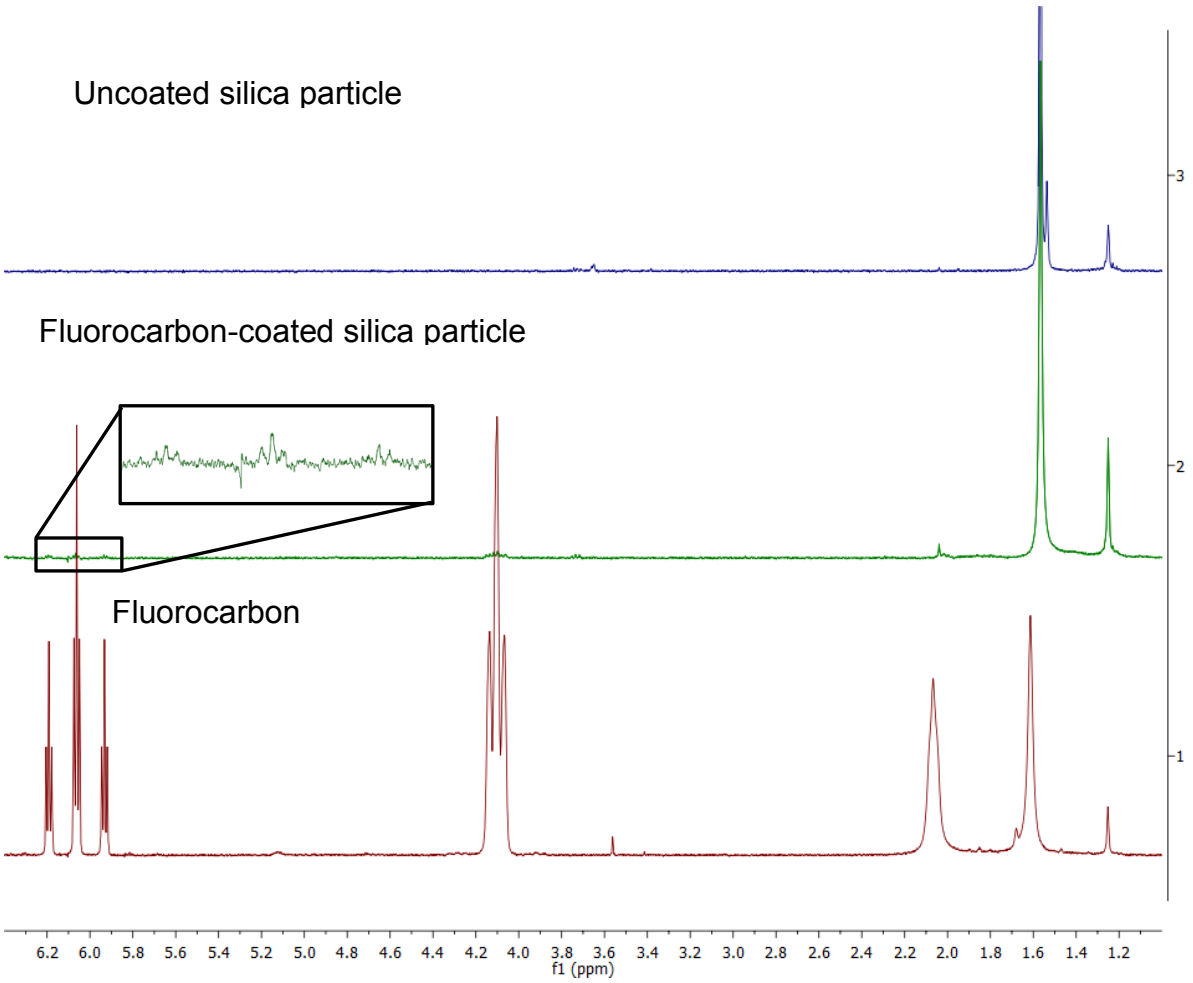

Figure S4. NMR spectrum of uncoated silica particles (top), fluorocarbon coated silica particles (middle) and 1H,1H,9H hexadecafluoro-1-nonanol (CAS 376-18-1, $C_9H_4F_{16}O$) (bottom) in $CDCl_3$.

Scanning Electron Microscopy (SEM)

The SEM image of dried, uncoated silica nanoparticles is recorded using JSM-7400F high resolution SEM in the Keck Microscope facility at the University of Delaware and is shown in Figure S5. This SEM image is analyzed by software ImageJ to measure the average nanoparticle radius. The average radius of the uncoated particles is 45.3 ± 5.3 nm which is in agreement with manufacturer.

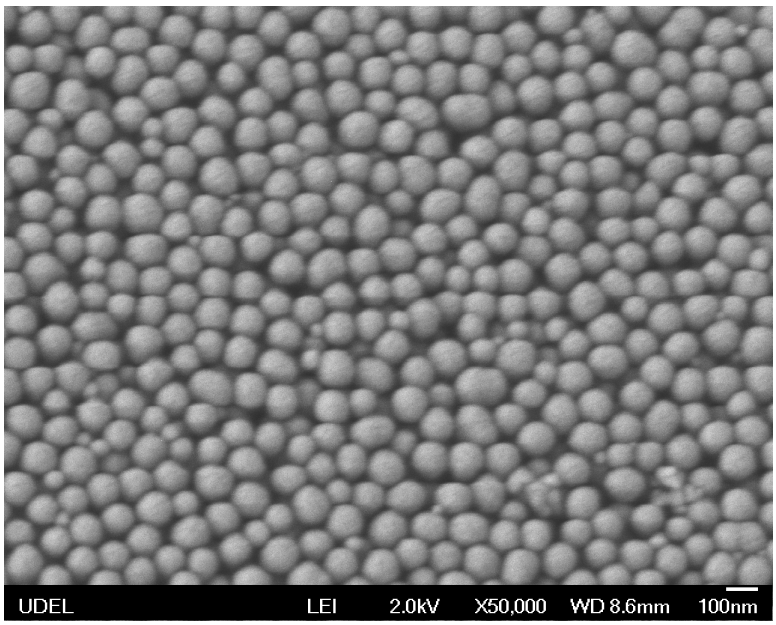

Figure S5. SEM image of dried, uncoated silica nanoparticles.

REFERENCES

1. Van Helden, A.; Jansen, J. W.; Vrij, A. Preparation and Characterization of Spherical Monodisperse Silica Dispersions in Nonaqueous Solvents. *Journal of Colloid and Interface Science* 1981, 81, 354-368.

2. Eberle, A. P.; Castañeda-Priego, R. N.; Kim, J. M.; Wagner, N. J. Dynamical Arrest, Percolation, Gelation, and Glass Formation in Model Nanoparticle Dispersions with Thermoreversible Adhesive Interactions. *Langmuir* 2012, 28, 1866-1878.

3. Iller, R. The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry. *New York, Cap* 1979, 1.