Nanoparticles Diffusion and Dispersion in Confined Pore Spaces with Oil Residuals

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This research project proposes to use an innovative nanostructure with precisely controlled orientations, dimensions, and surface properties – a slanted columnar thin film (SCTF) – to simulate the geometry of confined porous spaces, to study diffusion, dispersion, and attachment of nanoparticles in confined porous nanostructures during enhanced oil recovery. The diffusion, dispersion, and attachment of nanoparticles in SCTFs will be quantified and visualized using Generalized Ellipsometry (GE). The attachment of nanoparticles in SCTFs will also be measured using combined quartz crystal microbalance with dissipation and GE (QCM-D/GE).

Despite the PI's efforts to recruit a student to this project in the summer and fall of 2018, it was very difficult to find an excellent graduate research assistant to work on the project. The project was partially undertaken by one of PhD students, who also has responsibility to work on another project. In August 2019, a new PhD student joined the PI's research group, who will devote all his time to this project. The focus of the first year was on optimizing the methods of making SCTFs of various dimensions, measuring the attachment of nanoparticles in the SCTFs using QCM-D/GE, and analyzing the interaction energy between nanoparticles and SCTF surfaces.

Glancing angle deposition technique (GLAD) was used to make SCTFs. Si chips were placed inside the highly vacuumed GLAD chamber to evaporate at around 1.8×10^{-6} mbar, then deposited onto QCM-D sensor surfaces (QSX 301). The evaporated Si flux was incident upon the sample at 85°, which led to the Si-SCTF growth at an angle around 60° with respect to substrate normal. The deposition rate was kept at 1.5 Å/s, 2.5 Å/s, and 3.5 Å/s to grow 50 nm, 100 nm, and 200 nm thick Si-SCTFs, respectively. Finally, a conformal layer of alumina or silica, 4 nm thick, was deposited onto the Si-SCTF surface via atomic layer deposition (ALD) to form an Al_2O_3- Si-SCTF or SiO_2-Si-SCTF surface, respectively. Alumina- or silica-coated flat and SCTF model rough surfaces were used in this study to represent the most abundant silica reserve materials and metal-oxide impurities. SCTF surfaces were characterized using AFM, SEM, and GE. Particularly, GE measured geometric and optical properties of SCTFs, including thickness, slanting angle, slanting plane, and depolarization factors. GE characterizing data indicated that the produced SCTFs possess thickness and slanting angles are consistent with the expectation.

		50nm thick SCTF in water	100nm thick SCTF in water	100nm thick SCTF in 100mM NaCl	200nm thick SCTF in water
Structural Parameters	Thickness, H (nm)	56 ± 1	109 ± 2	106 ± 1	233 ± 3
	Slanting angle, Θ (°)	56 ± 1	54 ± 2	58 ± 1	60 ± 1
	Slanting plane, Φ (°)	213 ± 1	224 ± 1	240 ± 1	227 ± 1
Depolarization Factors	q_z	0.02 ± 0.00	0.11 ± 0.01	0.11 ± 0.01	0.17 ± 0.01
	q_{xy}	0.43 ± 0.01	0.41 ± 0.01	0.39 ± 0.01	0.4 ± 0.01
	f_{liquid} (%)	77 ± 1	75 ± 1	76 ± 1	82 ± 1
	f_{Si} (%)	23 ± 1	25 ± 1	24 ± 1	18 ± 1

QCM-D/GE experiments were conducted to measure the deposition of nanoparticles into SCTFs. An Explorer QCM-D system (Biolin Scientific AB, Stockholm, Sweden) was mounted to an M-2000 spectroscopic ellipsometer (J.A. Woollam, Co., Inc., Lincoln, NE) stage to form a combined QCM-D/GE system. Prior to QCM-D/GE experiments, the prepared QCM-D sensors were first oxygen-plasma-cleaned inside the ALD chamber. The QCM-D sensors were then mounted within the QCM-D chamber, which contains windows at a 65° angle of incidence with respect to the substrate normal for the probing light beam of an ellipsometry measurement. It should be noted that QCM-D sensors were positioned inside the flow channel with the contact electrodes always perpendicular to the probing light beam plane of incidence. Before running the QCM-D experiments, the rough QCM-D sensors were characterized by GE to determine the structural properties of SCTFs. "Blank solution" (either ultra-pure water or 100 mM NaCl at pH 7 ± 0.1) was then introduced into the QCM-D flow chamber at a flow rate of 0.1 mL/min (Phase I) to reach a baseline (normalized frequency drift < 0.25 Hz/hr). Then in-situ GE and QCM-D measurements
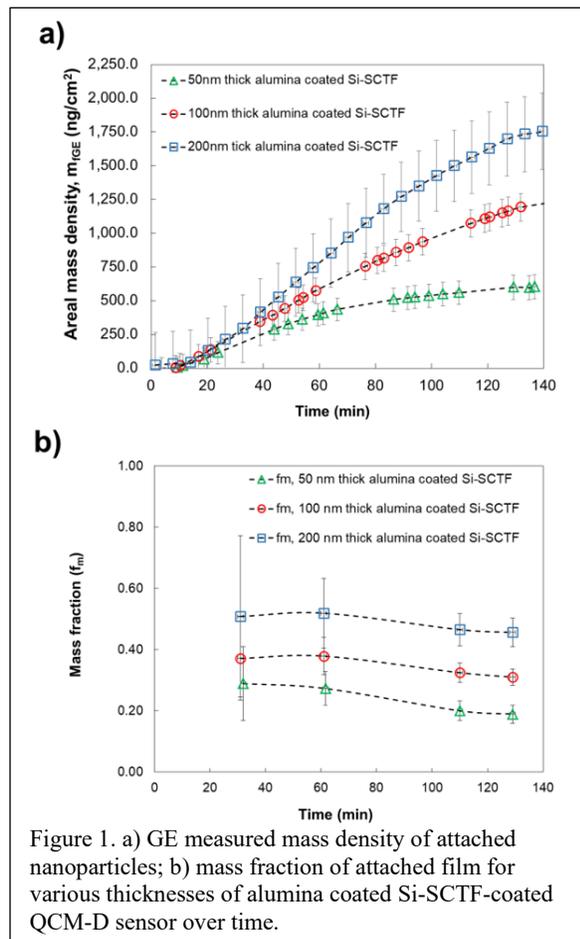
Figure 1. a) GE measured mass density of attached nanoparticles; b) mass fraction of attached film for various thicknesses of alumina coated Si-SCTF-coated QCM-D sensor over time.

were set to start simultaneously. 5 ppm nanoparticle suspension was then introduced into the flow chamber (Phase II) with the same ionic strength of the blank solution and at the same flow rate of 0.1 mL/min. Nanoparticle in ultra-pure water or 100 mM NaCl was introduced for 120 min. We found that no attachment of nanoparticles onto the rough 100 nm thick SiO_2-Si-SCTF surface. Our experiments demonstrated that the presence of surface roughness (ca. 100 nm) by itself was not enough to overcome the unfavorable conditions for 15 nm nanoparticles in ultra-pure water. Under the favorable condition, we observed an increase of attachment with the increase of SCTF dimension. After about 20 minutes of exposure to nanoparticles, QCM-D measured deposition reached 662 ng/cm^2, 669 ng/cm^2, and 773 ng/cm^2 and continued to increase to 3142 ng/cm^2, 3753 ng/cm^2, and 4615 ng/cm^2 after 130 min for 50 nm, 100 nm, and 200 nm thick Al_2O_3-Si-SCTF-coated QCM-D surfaces, respectively. Simultaneous GE measurements, which provided only the dry mass of nanoparticles attached to SCTF surfaces, was 597 ng/cm^2, 1176 ng/cm^2, and 1754 ng/cm^2, for 50nm, 100nm, and 200 nm respectively. We also found that the mass fraction of the attached nanoparticle layer increased with increasing height of SCTFs, which could be attributed to increased surface coverage of nanoparticles on the thicker SCTF layers.

The interaction energy between spherical nanoparticles and a rough ellipsoidal collector surface was calculated using the surface element integration (SEI) method. In this method, the total interaction energy is computed between two bodies by integrating the interaction energy over the exact geometry of the interacting surfaces. As a first step, SCTF was simplified as an ellipsoidal asperity.

Interactions between a nanoparticle and ellipsoidal SCTF surface and between nanoparticles and a flat base surface were considered. For these calculations, the surface charge of the thin alumina and silica ALD layers were chosen as 25 mV and -42 mV, respectively; these values were based on a previous experimental study of alumina and silica ALD layers on silicon wafers at pH 7 in 1 mM KCl, which are similar experimental conditions. Figure 2 provides some example DLVO analysis results.
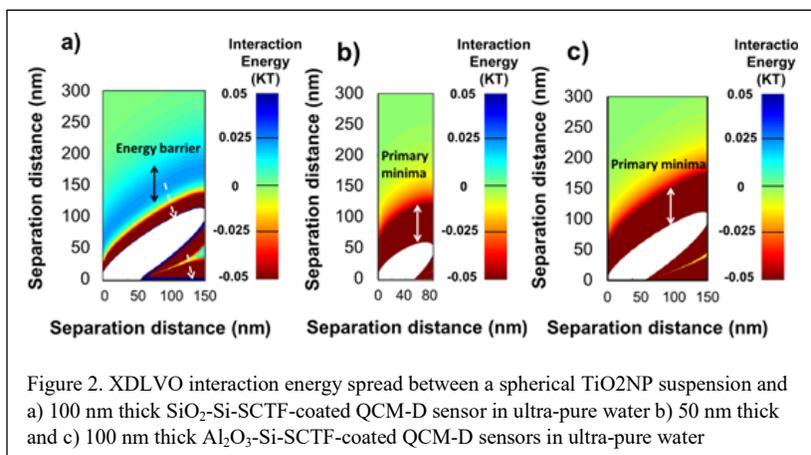

Figure 2. XDLVO interaction energy spread between a spherical TiO2NP suspension and a) 100 nm thick SiO_2-Si-SCTF-coated QCM-D sensor in ultra-pure water b) 50 nm thick and c) 100 nm thick Al_2O_3-Si-SCTF-coated QCM-D sensors in ultra-pure water