Supporting Information for

The Predominant Effect of Material Surface Hydrophobicity on Gypsum Scale Formation

Xiaochuan Huang [a,b], Chen Li [a,c], Kuichang Zuo [a,b], Qilin Li [a,b,]*

[a]Department of Civil and Environmental Engineering, Rice University, MS-519, 6100 Main Street, Houston 77005, United States

[b]NSF Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, Rice University, MS-6398, 6100 Main Street, Houston 77005, United States

[c]School of Environment, Tsinghua University, Beijing 100084, China

*Corresponding author:

Qilin Li, Email: qilin.li@rice.edu, Phone:713-348-2046

Kuichang Zuo, Email: kuichang.zuo@rice.edu, Phone:832-230-7547

6 Pages, 5 Text Sections, 3 Tables, 5 Figures

Supplemental materials

Text S1. The fabrication of gold-coated silicon chips

Before Au coating, silicon chips were sonicated sequentially in acetone, methanol and isopropanol solutions each for 15 min and dried with ultra-pure N_2.[1] Clean Si chips were then coated with a 5-nm Ti layer followed by a 10-nm Au layer using a sputter coater (Denton Desk V Sputter system, Denton Vacuum).

Text S2. The cleaning procedure of QCM sensors and substrates

All substrates were cleaned thoroughly immediately before SAM preparation. The gold QCM sensors and gold-coated silicon chips were cleaned sequentially in toluene, acetone and ethanol in a sonication bath, twice in each solution for 10 min each time.[1] After thorough rinsing with MilliQ water and dried with ultra-pure N_2 gas, they were further cleaned with a UV/Ozone cleaner (UV/Ozone ProCleaner, Bioforce Nanosciences) for 30 min. SiO_2 QCM sensors and glass slides were first cleaned in the UV/Ozone chamber for 10 min, and then immersed in 2% SDS solution for 30 min at room temperature. After thorough rinsing with MilliQ water and dried with ultra-pure N_2 gas, they were treated with the UV/Ozone cleaner for another 10 min. The water contact angles were used as a quick check for the formation of SAMs. For clean gold chips and glass slides, the surfaces were extremely hydrophilic with contact angles of less than 20°. (Figure S1)

Text S3. Calculation the surface tension components of each substrates.

The surface tension components of the substrates were calculated by the following equation[2],

$$(1+\cos\theta)\gamma_l = 2(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}) \quad \text{(S1)}$$

Where, *l* and *s* stand for liquid and substrate; *cosθ* was calculated form measured contact angle between the respective liquid and the substrate (Figure S2). The calculated surface tension components were reported in Table S3.

Text S4. The hydration energy ΔG_{ls} between liquid *l* and substrate *s* is calculated by the following equation,

$$\Delta G_{ls} = -\gamma_l (1 + \cos\theta) \tag{S2}$$

Text S5. The deduction of equation (3) in the manuscript when the γ_n^+ and γ_s^+ are negligible.

$$\gamma_{ns} = (\sqrt{\gamma_n^{LW}} - \sqrt{\gamma_s^{LW}})^2 + 2(\sqrt{\gamma_n^+\gamma_n^-} + \sqrt{\gamma_s^+\gamma_s^-} - \sqrt{\gamma_n^+\gamma_s^-} - \sqrt{\gamma_n^-\gamma_s^+}) \approx (\sqrt{\gamma_n^{LW}} - \sqrt{\gamma_s^{LW}})^2 \tag{S3}$$

$$\gamma_{ls} = (\sqrt{\gamma_l^{LW}} - \sqrt{\gamma_s^{LW}})^2 + 2(\sqrt{\gamma_l^+\gamma_l^-} + \sqrt{\gamma_s^+\gamma_s^-} - \sqrt{\gamma_l^+\gamma_s^-} - \sqrt{\gamma_l^-\gamma_s^+}) \approx (\sqrt{\gamma_l^{LW}} - \sqrt{\gamma_s^{LW}})^2 + 2(\sqrt{\gamma_l^+\gamma_l^-} - \sqrt{\gamma_l^+\gamma_s^-}) \tag{S4}$$

$$\begin{aligned}\gamma_{ns} - \gamma_{ls} &\approx (\sqrt{\gamma_n^{LW}} - \sqrt{\gamma_s^{LW}})^2 - (\sqrt{\gamma_l^{LW}} - \sqrt{\gamma_s^{LW}})^2 - 2(\sqrt{\gamma_l^+\gamma_l^-} - \sqrt{\gamma_l^+\gamma_s^-}) \\ &= \gamma_n^{LW} - \gamma_l^{LW} - 2\sqrt{\gamma_s^{LW}}(\sqrt{\gamma_n^{LW}} - \sqrt{\gamma_l^{LW}}) + 2\sqrt{\gamma_s^-}\sqrt{\gamma_l^+} - 2\sqrt{\gamma_l^+\gamma_l^-}\end{aligned} \tag{S5}$$

Table S1. the detailed characteristics of -OH, $-CH_3$ and $-CF_3$ terminated SAMs

Terminal group	functionalized thiol/silane	Contact angle (°)	Roughness (nm)	Elemental ratio by XPS: O:C ratio	F:C ratio	S:C ratio
-OH	$HS\text{-}(CH_2)_{11}OH$	45.3±5.1	0.6±0.06	0.08 (0.09)*	-	0.07 (0.08)*
$-CH_3$	$HS\text{-}(CH_2)_{11}CH_3$	105.1±0.9	0.7±0.06	-	-	0.05 (0.08)*
$-CF_3$	$(CH_3CH_2)_3O_3Si\text{-}(CH_2)_2(CF_2)_7CF_3$	119.2±1.2	0.9±0.07	-	1.22 (1.06)*	-

* Theoretical elemental ratio based on molecular formula.

Table S2. the surface tension components of the three probe liquids[2]

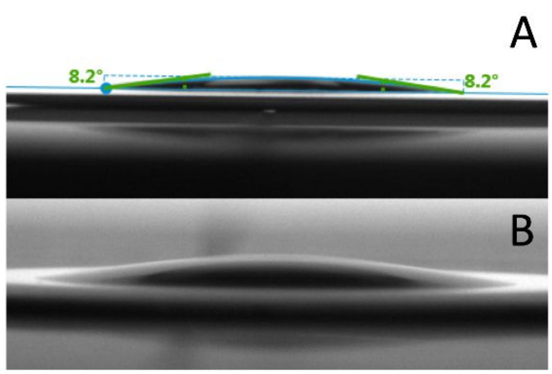
	γ_l	γ^{LW}	γ^{AB}	γ^+	γ^-
Water	72.8	21.8	51	25.5	25.5

Diiodomethane	50.8	50.8	0	0	0
Ethylene glycol	48	29	19	1.92	47

Table S3. the surface tension components of gypsum and SAMs calculated from contact angles measurements

	γ^{T}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
$-CF_3$	9.82	9.52	0.29	0.061	0.35
$-CH_3$	25.22	25.08	0.14	0.33	0.015
-OH	45.46	41.42	4.04	0.11	35.89
$CaSO_4$*	47.76*	47.14*	0.62*	0.002*	47.87*

* Values were of gypsum freshly cleaved from selenite plane, adopted from Teng *et al*[3]



n

Figure S1. Water contact angles of sensors. The contact angle of clean gold sensor (A) and SiO_2 sensor (B).

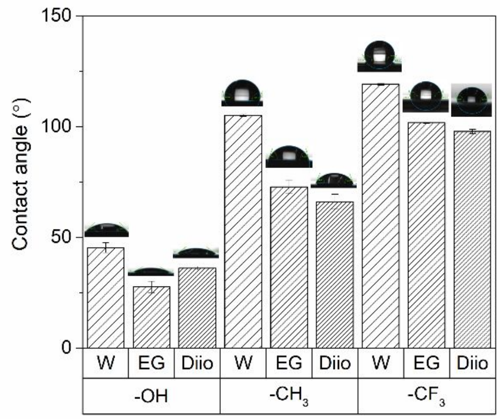


Figure S2. Contact angles of water(W), ethylene glycol (EG) and diiodomethane (Diio) on different SAMs.

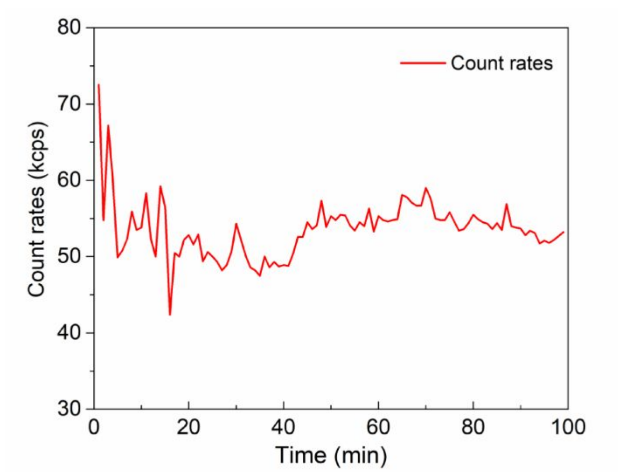


Figure S3. the light scattering intensity of 25 mM $CaSO_4$ solution over time.

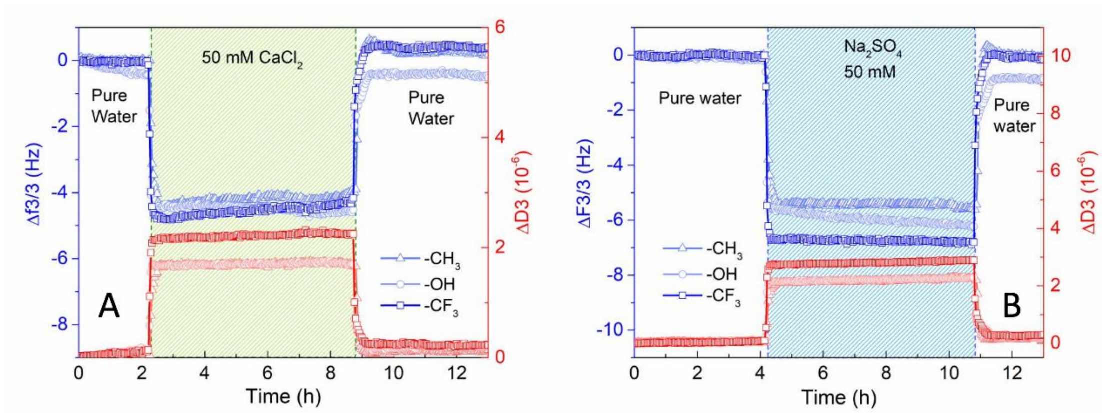


Figure S4. the reversible adsorption on different SAMs of $CaCl_2$ (A) and Na_2SO_4 (B) in short experiment period.

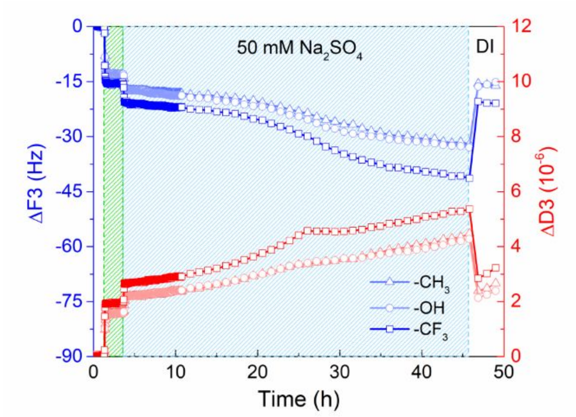


Figure S5. Repeat experiment results of ion-induced gypsum nucleation.

REFERENCES

1. Steiner, Z.; Rapaport, H.; Oren, Y.; Kasher, R., Effect of surface-exposed chemical groups on calcium-phosphate mineralization in water-treatment systems. *Environ Sci Technol* **2010,** *44*, 7937-7943.
2. Oss, C. J. v., *Interfacial forces in aqueous media*. 2nd ed.; Taylor & Francis Group: United States of America 2006.
3. Teng, F.; Zeng, H.; Liu, Q., Understanding the deposition and surface interactions of gypsum. *The Journal of Physical Chemistry C* **2011,** *115* (35), 17485-17494.