Electronic Supplementary Information (ESI)

Ice nucleation on nanotextured surfaces: Influence of surface fraction, pillar height and wetting states

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Local bond orientational oder parameter analysis

In order to detect ice-like molecules, we have used the *CHILL* algorithm of Moore et al.[1] which is based on an order parameter by distinguishing between liquid- and ice-like local arrangements around each water molecule. The local orientational order parameter $q_{lm}^{(i)}$ around each water molecule i is defined as

$$q_{lm}^{(i)} = \frac{1}{4}\sum_{j=1}^{4} Y_{l,m}(\hat{r}_{ij}) \tag{1}$$

The correlation $d_l^{(ij)}$ between the nearby neighboring molecules i and j is measured by the normalized dot product of $\mathbf{q}_l$ vectors with the same l-value.

$$\begin{aligned} d(i,j) &= \frac{q_l^{(i)} \cdot q_l^{(j)}}{|q_l^{(i)}||q_l^{(j)}|} \\ &= \frac{\sum_{m=-l}^{l} q_{lm}^{(i)} q_{lm}^{*(j)}}{(\sum_{m=-l}^{l} q_{lm}^{(i)} q_{lm}^{*(i)})^{1/2} (\sum_{m=-l}^{l} q_{lm}^{(j)} q_{lm}^{*(j)})^{1/2}} \end{aligned} \tag{2}$$

In simulations, $l = 3$ or 6 (i.e. the order parameters q_3 or q_6) are mostly used to identify the ice-like molecule from supercooled water[1–3]. Here we have used $l = 3$ to distinguish ice crystals (cubic I_c and hexagonal I_h) from liquid and interfacial ice or intermediate ice. According to *CHILL* algorithm, a molecule in ice I_c has all its four closest neighbors involved in a staggered structure and the $d(i,j)$ value is less than -0.8. In hexagonal ice phase, a molecule has one an eclipsed arrangement (-0.2 < d < -0.05) with its one of the four closest neighbors, whereas others three bonds are found in the same staggered structure as in cubic ice (d < -0.8.) In addition, Moore et al.[1] defined interfacial or intermediate-ice I where each water molecule has local ordering intermediate between that of ice crystals (cubic or hexagonal) and liquid. An intermediate-ice molecule has only two staggered configurations and at least one neighbor with greater than two staggered bonds or three staggered bonds, no eclipsed bond and at least one neighbor with two staggered arrangements. The size of the largest cluster is defined by clustering the ice crystals and intermediate ice using 0.35 nm cut-off distance.

Mean first-passage time (MFPT) method

We have used the mean first-passage times (MFPT) method as proposed by Wedekind et al.[4] to determine the nucleation rate. The MFPT method directly provides the nucleation time and the size of the critical nuclei by fitting the MFPT curve using the following expression:

$$\tau(n) = \frac{\tau_J}{2}\{1 + erf[(n - n^*)\, c]\} \tag{3}$$

where τ_J and n^* are the nucleation time and the critical nuclei size respectively. The parameter c is a constant which is related to Zeldovich factor, Z as $c = Z\sqrt{\pi}$. The nucleation time $\tau(n)$ is obtained for each cluster size n by averaging time over several nucleation simulations with different initial configurations. Figure S1 plots the MFPT as a function of cluster size obtained from MD simulation and the corresponding fit to equation (3). The nucleation rate J is estimated from the volume V of the water and the time of nucleation τ_J, $J = 1/(\tau_J V)$. The critical cluster size, n^* is obtained simply by fitting the MFPT using equation (3).

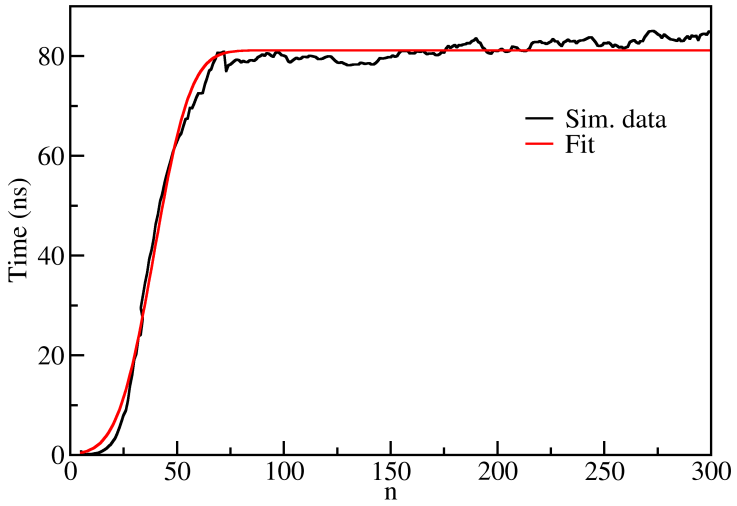

Figure S1: Plot of the MFPT curve for a water cylinder on nanostructured surface (black line). The red line is fit to eq. (3)

Calculation of work of adhesion

We have employed the phantom-wall method[5] in order to compute the work required to remove the ice droplet from nanostructured surfaces having different roughness. In the phantom wall method, the free energy difference (ΔF) between the initial and the final states is evaluated as:

$$\Delta F = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle d\lambda \tag{4}$$

The state $\lambda = 0$ corresponds to the water interact only with nanostructured surface (actual system); whereas the water interact only with the phantom wall (reference system) at the state $\lambda = 1$. U(λ) is the potential energy of the system which is depends on a coupling parameter λ as follows:

$$U(\lambda) = (1 - \lambda)\, U^{Struct.} + \lambda U^{ref.}. \tag{5}$$

In the present study, we have considered the graphite-like flat (smooth) surface as a reference system, which interacts with water via a purely repulsive Weeks-Chandler-Andersen (WCA) potential[6]. The schematic representation is shown in Figure S2

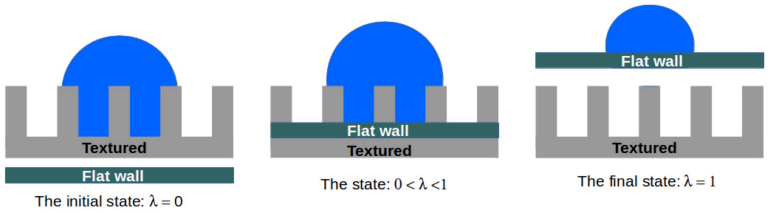

Figure S2: Schematic representations of the thermodynamic integration process. In the initial state ($\lambda = 0$), the water interacting only with the structured (actual) surface. The state $0 < \lambda < 1$ corresponds to the water interacting with both the structured surface and the flat wall (reference system). In the final state ($\lambda = 1$), the water interacting only with the flat wall (reference system).

We have performed MD simulations for different values of λ to calculate $\frac{\partial U(\lambda)}{\partial \lambda}$ and obtain ΔF by numerical integration The average ΔF value is estimated by performing of 4-6 independent simulations.

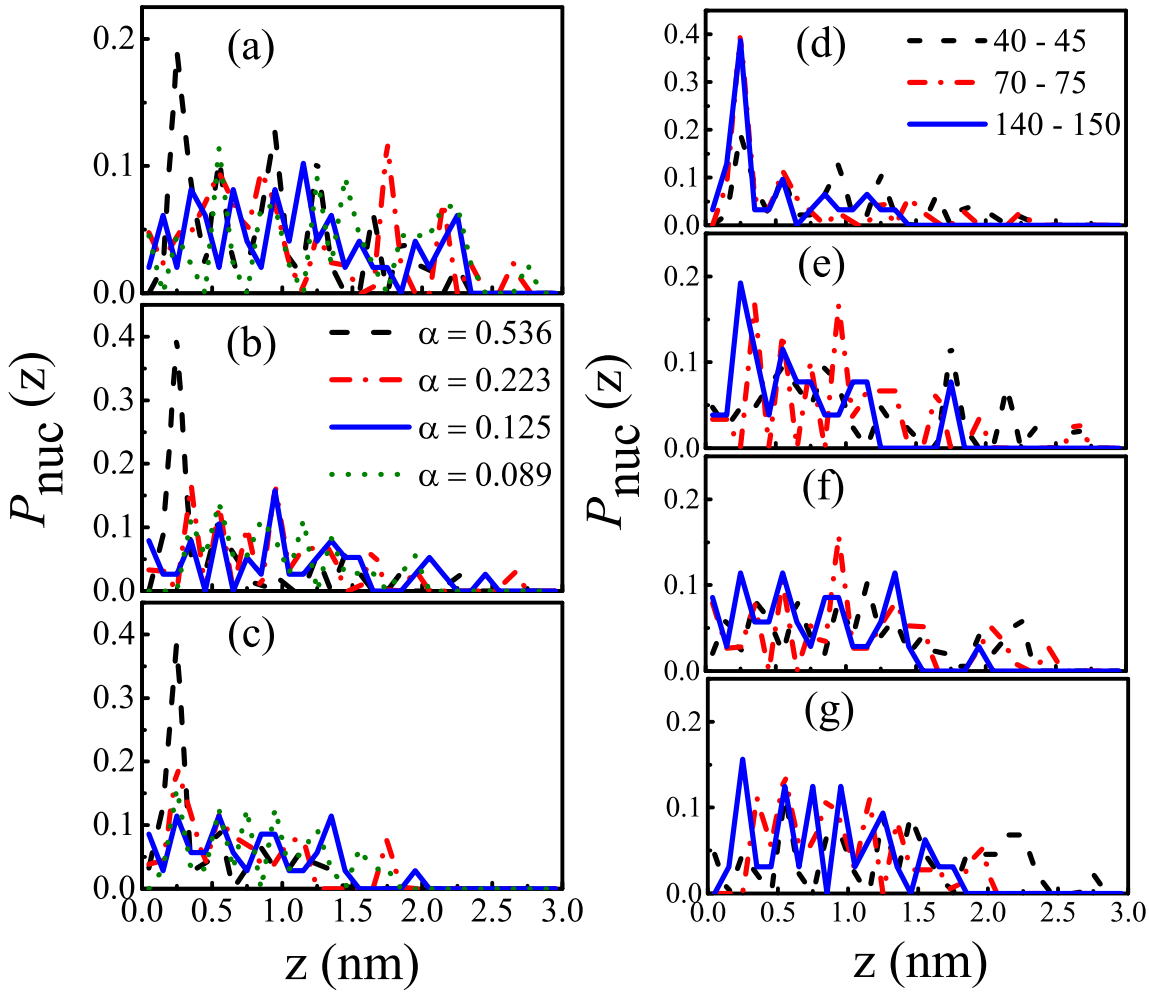

Figure S3: Probability distribution $P_{nuc}(z)$ of center of mass of the z-coordinate of ice clusters along the z-axis from the top of the nanostructured surfaces. The right panel shows the corresponding distribution of cluster size at different stages of ice crystallization: (a) 40-45, (b) 70-75, and (c) 140-150. The right panel shows the probability distribution of different clusters for different nanostructured surfaces: (d) $\alpha = 0.536$, (e) $\alpha = 0.223$, (e) $\alpha = 0.125$, and (f) $\alpha = 0.089$.

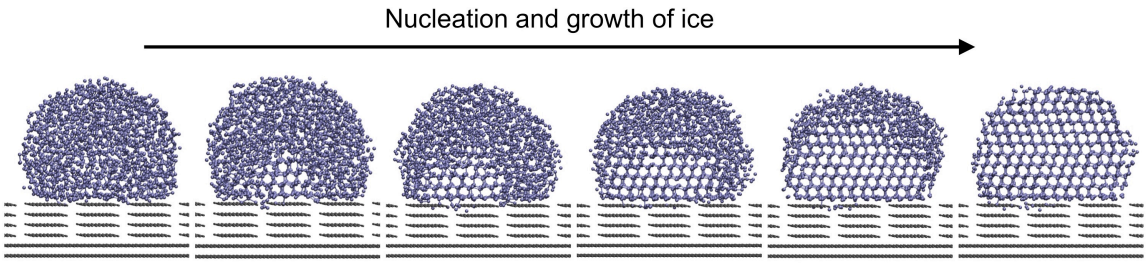

Figure S4: Snapshots along the progress of crystallization for $\alpha = 0.536$. Surface atoms and water molecules are shown as gray and ice blue balls, respectively. The ice-like molecules are connected by sticks.

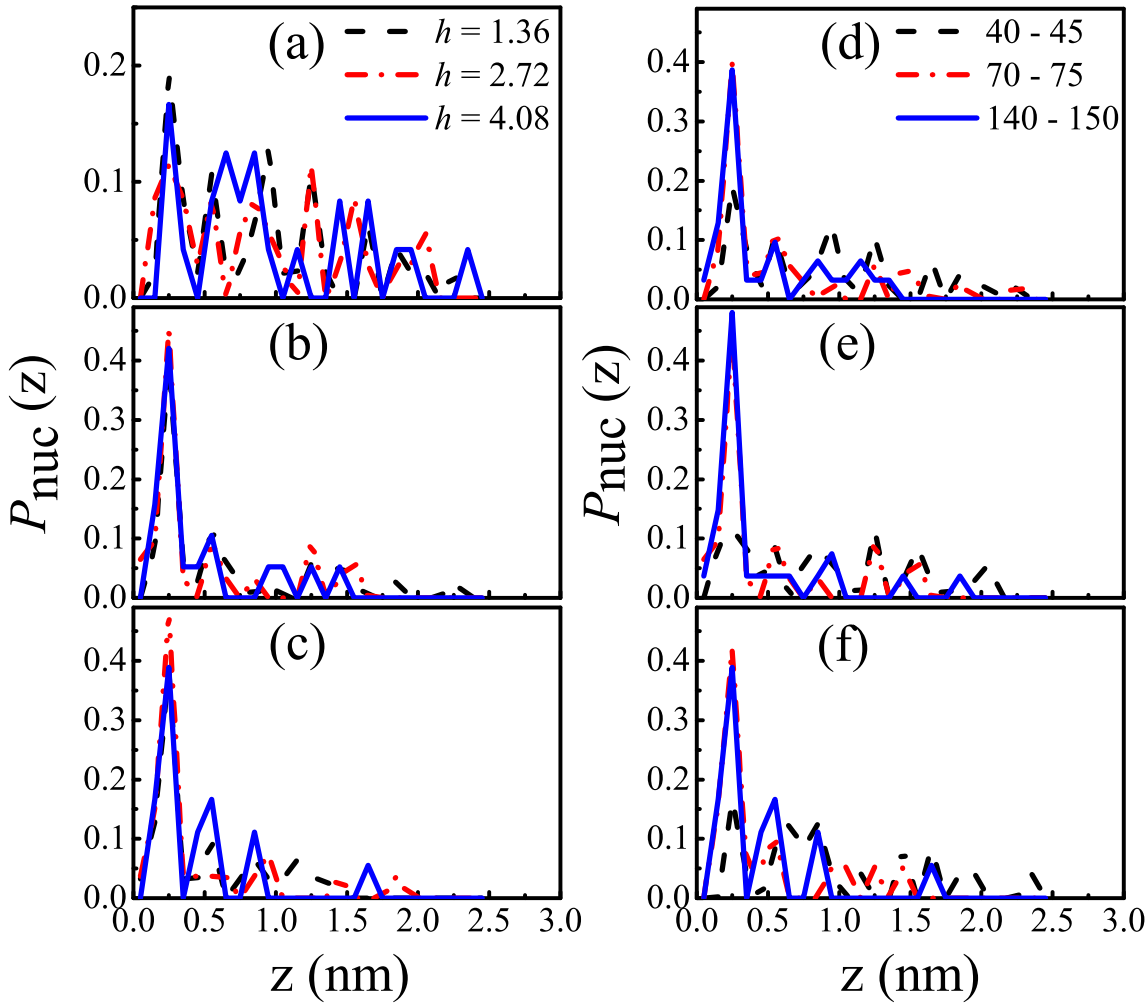

Figure S5: Probability distribution $P_{nuc}(z)$ of center of mass of the z-coordinate of ice clusters along the z-axis from the top of the nanostructured surface for $\alpha = 0.536$. The right panel shows the corresponding distribution of cluster at different stages of ice crystallization: (a) 40-45, (b) 70-75, and (c) 140-150; . The right panel shows the probability distribution of different clusters for different heights of the nanostructured surfaces: (d) $h = 1.36$ nm, (e) $h = 2.72$, and (f) $h = 4.08$.

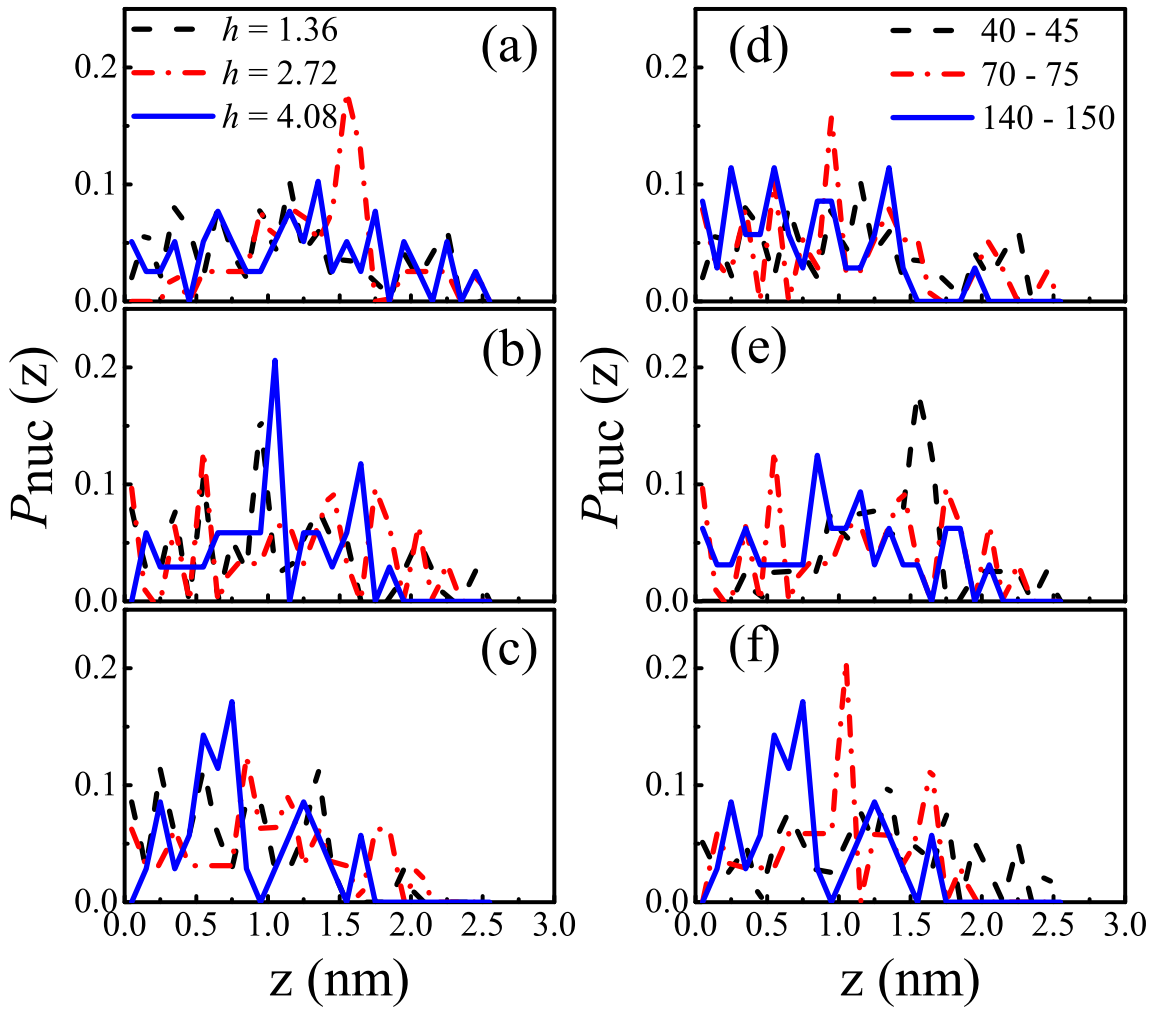

Figure S6: Probability distribution $P_{nuc}(z)$ of center of mass of the z-coordinate of ice clusters along the z-axis from the top of the nanostructured surface for $\alpha = 0.125$. The right panel shows the corresponding distribution of cluster at different stages of ice crystallization: (a) 40-45, (b) 70-75, and (c) 140-150; . The right panel shows the probability distribution of different clusters for different heights of the nanostructured surfaces: (d) $h = 1.36$ nm, (e) $h = 2.72$, and (f) $h = 4.08$.

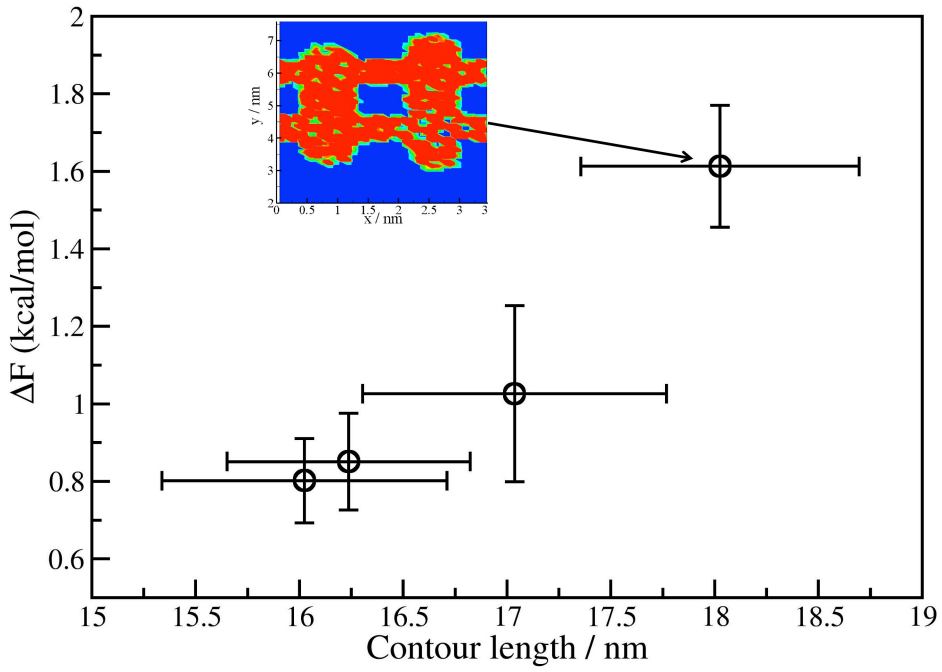

Figure S7: The surface free energy difference (ΔF) as a function of roughness contour length for the case of Wenzel wetting states.

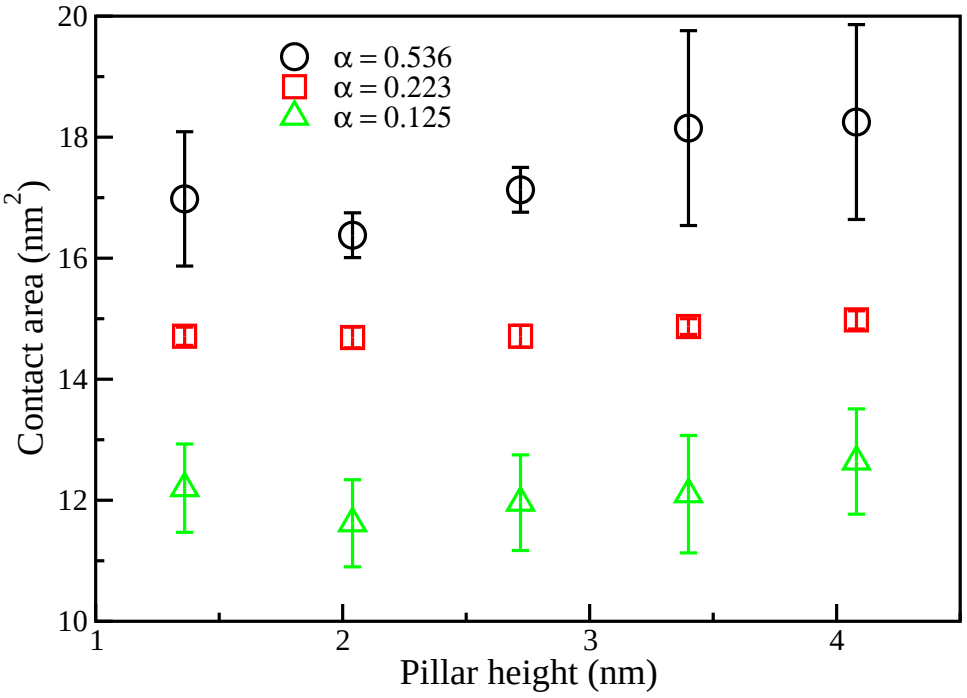

Figure S8: The base contact area as a function of pillar height for $\alpha = 0.536$, 0.223, and 0.125.

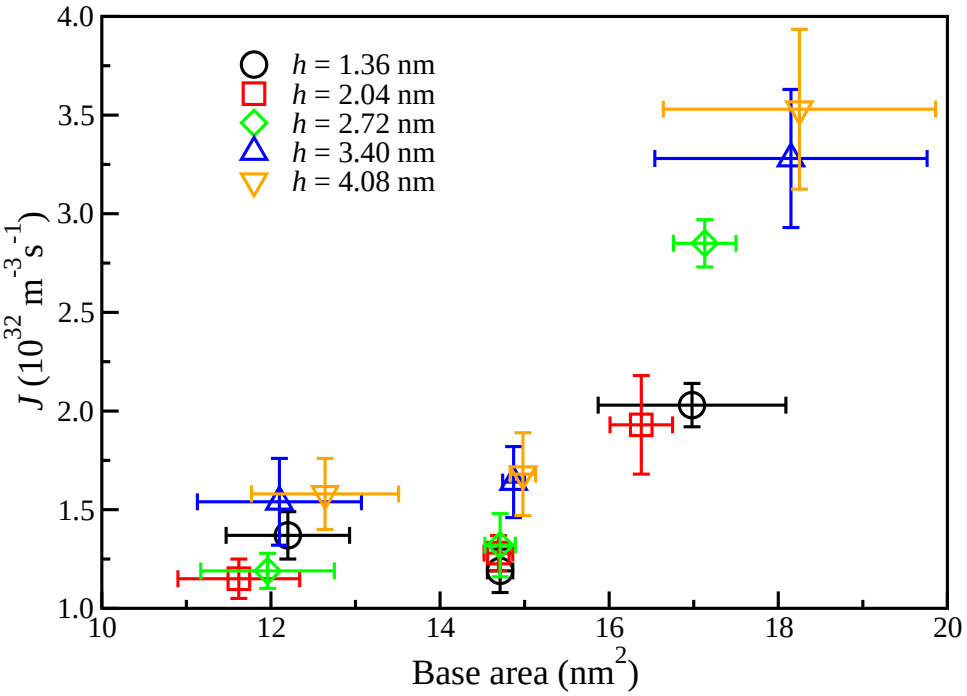

Figure S9: Variation of the rate of nucleation with contact area for the different nanostructured surfaces (α = 0.536, 0.223, and 0.125).

References

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