

*Supplementary Information*

**Selective nucleation of ice crystal depending on the inclination  
angle of nanostructure**

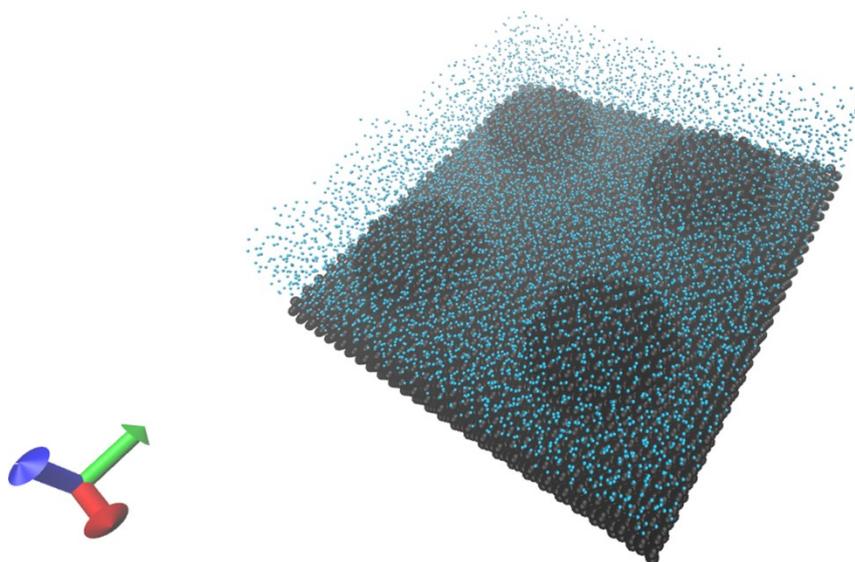
Yangjiangshan Xu<sup>a</sup>, Yizhou Shen<sup>a</sup>, Jie Tao<sup>a,\*</sup>, Yang Lu<sup>a</sup>, Haifeng Chen<sup>b</sup>, Wenqing Hou<sup>a</sup>, Biao Jiang<sup>a</sup>

<sup>a</sup> College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China

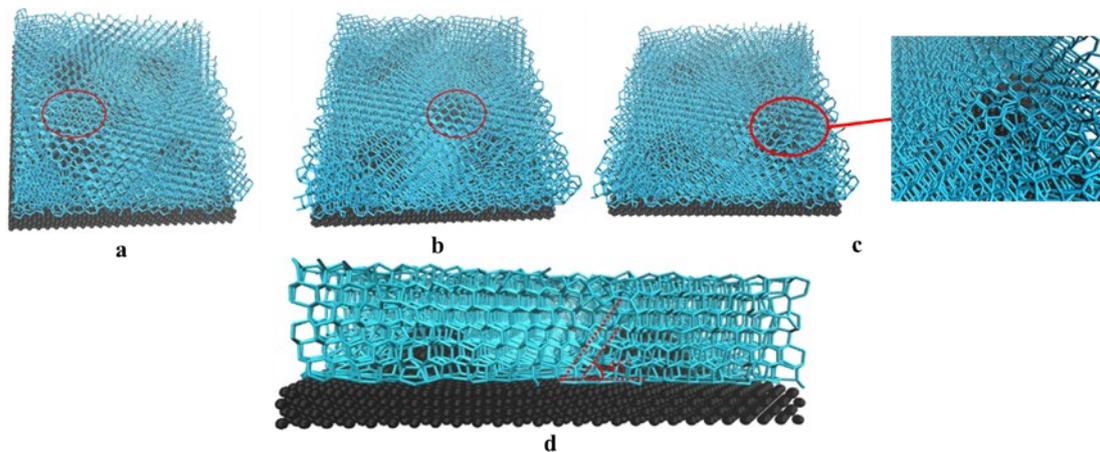
<sup>b</sup> Department of Materials Chemistry, Qiuzhen School, Huzhou University, 759, East 2nd Road, Huzhou 313000, P. R. China

\* Corresponding author: Prof. Jie Tao,

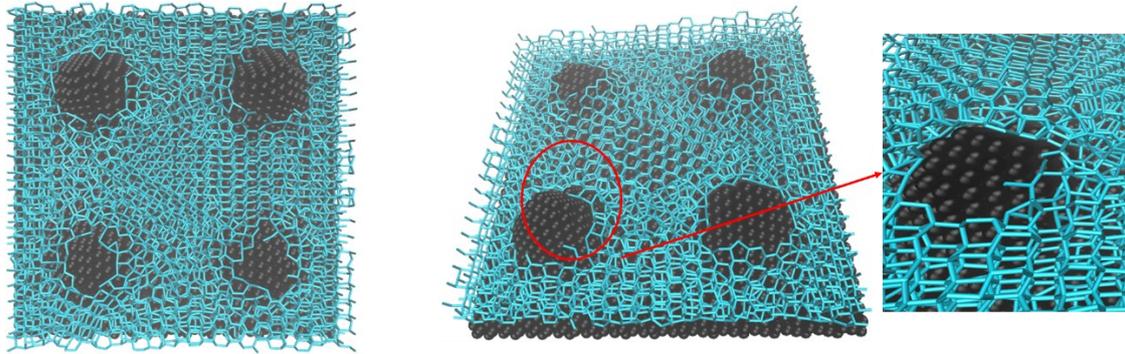
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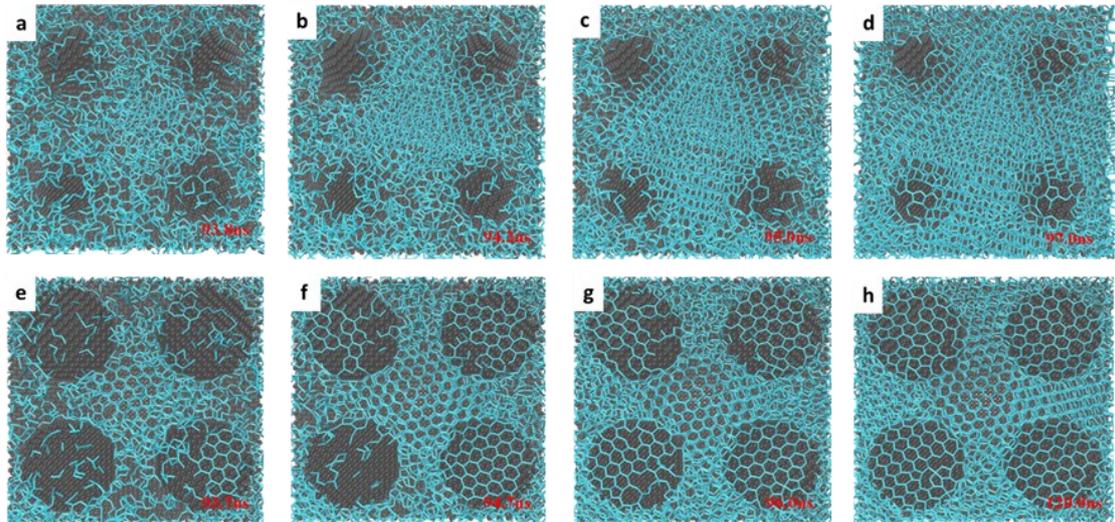
**Supplementary Figure S1. A typical simulation cell.** Water slab is put on the nanorods with different inclinations. A periodic boundary condition is applied to the simulation cell on three directions. The dimension of cell along z axis is 300Å to make sure that water molecules are only effected by one substrate. Atoms of substrates and water molecules are colored by black and cyan, respectively.



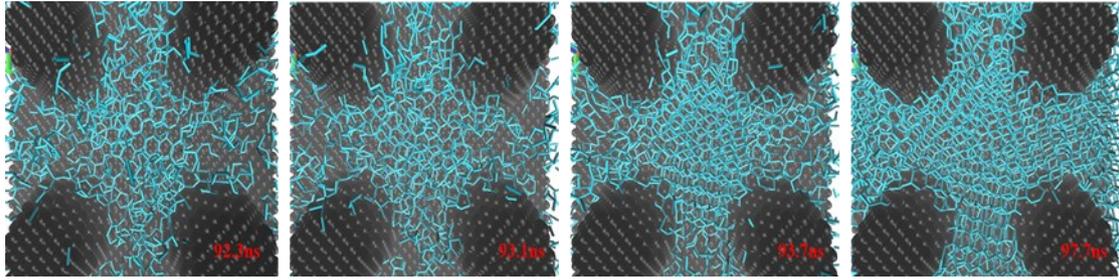
**Supplementary Figure S2. Icing result on 45° nanorods.** (a-c) 45° viewing of the simulation cell.  $I_c$  is the dominant part of ice crystal in the interspace of nanorods structures (shown in a and b) and near the nanorods structures (shown in fig c). (d) Side viewing of the simulation cell. The inclination of ice crystal is matching with the 45° nanorods structures.



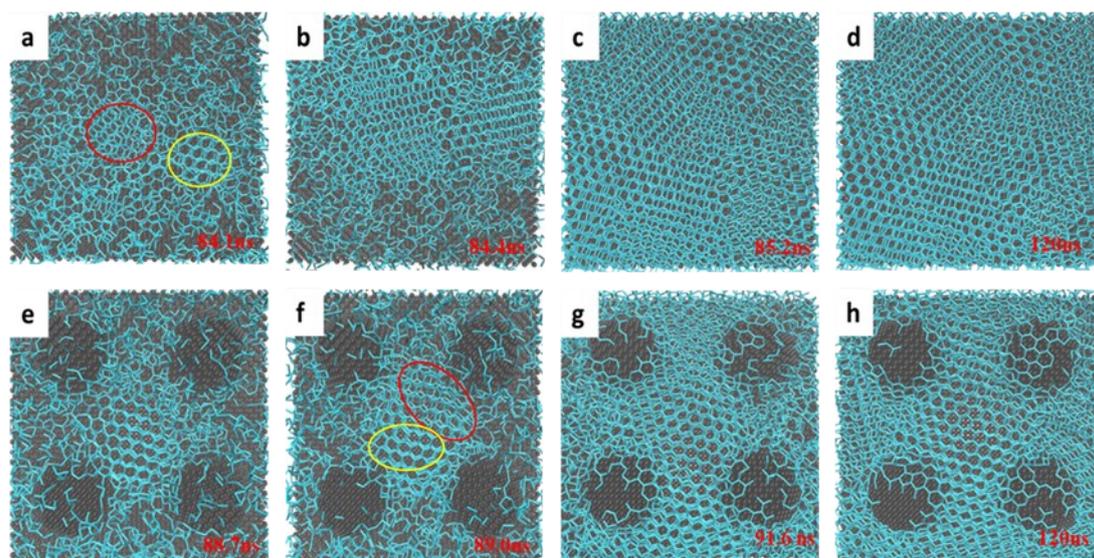
**Supplementary Figure S3. Icing results on FCC (211) face.** Pure  $I_h$  is formed on flat FCC (211) face,<sup>1</sup> however under the influence of  $45^\circ$  nanorods, the cubicity of ice crystal is obviously increased. Furthermore, ice crystal near the nanorods structures fits the structures well, and ice crystal grows along the nanorods, indicating that nanorods play important roles in the nucleation. The specific cubicity is hard to be calculated, because there are too many defects in the ice crystal.



**Supplementary Figure S4. The complete icing processes on 45° and 90°-inclination nanorods.** (a-d). The icing process on 45°-inclination nanorods. I<sub>c</sub> crystal is formed on such nanostructures, and fits the nanorods structures entirely. (e-h) The icing process on 90°-inclination nanorods. The icing result on 90°-inclination nanorods is exactly opposite of that on 45°-inclination nanorods. It is almost I<sub>h</sub> formed, and ice crystal arranges regularly.

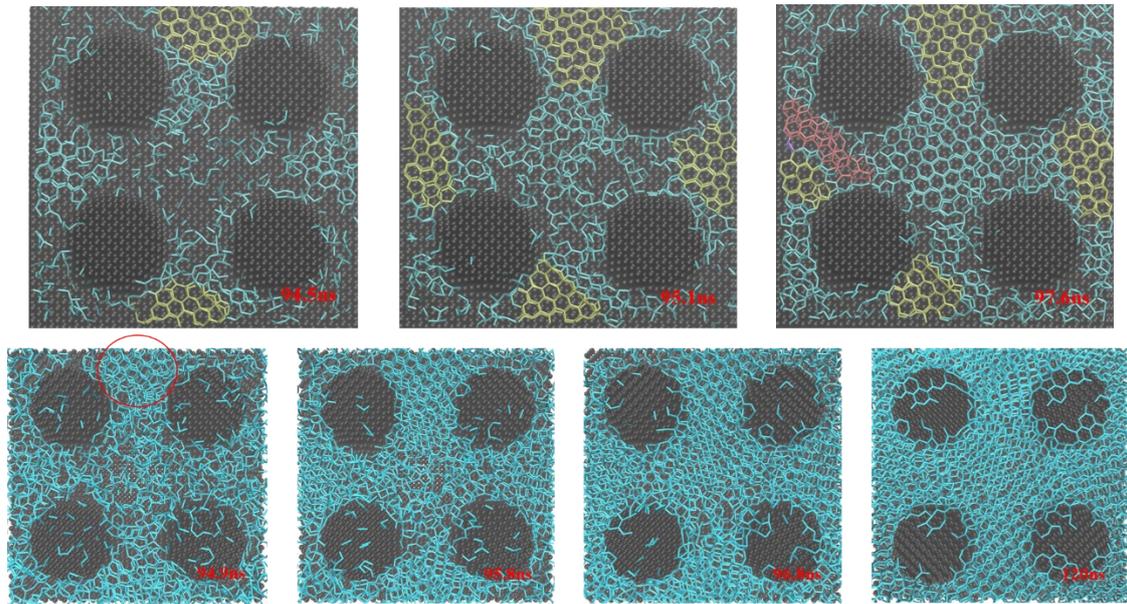


**Supplementary Figure S5. Icing process on higher 60°-inclination nanorods.** The heights of nanorods structures are fixed at 1.8nm. According to the equation in the paper, the space is enough for  $I_c$  to construct the horizontal relative displacement between layers of water molecules, so that the final ice crystal is  $I_c$  with high cubicity about 0.74.



**Supplementary Figure S6. Complete icing processes on flat substrate and 60°-inclination nanorods.** (a-d) The icing process on flat substrate. Only five layers of water molecules are shown because if observing the whole molecules, pictures will be difficult to be distinguished. As it is mentioned in paper, disordered stacking ice is formed on flat substrate. Note that not only one initial ice nucleus is formed at the beginning of the nucleation process. Red circle in Fig. (a) is I<sub>c</sub> nucleus, and yellow circle is I<sub>h</sub> nucleus, which means that there is no obvious trend of selective nucleation during the nucleation process on flat surface. (e-h) The icing process on 60°-inclination nanorods. The ice crystal formed on 60°-inclination is also disordered stacking ice, but some obvious defects appear in the interspace of two nanorods structures. Red circle in fig (f) is I<sub>c</sub> near the nanorods structures, and the yellow circle is I<sub>h</sub> far away from the nanorods. Note that I<sub>c</sub> does not appear near every nanorod, the reason may be complex and we consider that there are two main reasons. The first one is that the icing is a random process, meanwhile the 60°-inclination nanorods cannot provide enough constraint, which causes randomness in icing results. The second one is that our system

is small relatively, and the relative displacement space has been compensated by the  $I_c$  near other nanorods structures.



**Supplementary Figure 7. Icing process on 75°-inclination nanorods.** Cyan lattices are water atoms, yellow lattices represent the  $I_h$ , red lattices are  $I_c$  and black balls are the atoms of substrates. The initial ice nucleus is created at the bound of the system, and it is difficult to observe the change of ice crystal. It is not sure whether others factors effects the nucleation process on 75° inclination nanorods. It is found that the initial ice nucleus is pure  $I_h$ , causing the low freezing efficiency on 75°-inclination nanorods.

## Supplementary Note 1: Water model

Interaction among water molecules was described by the monatomic water model mW,<sup>2</sup> and LJ potential is used to define the force between water molecules and substrates atoms.<sup>1</sup> mW is a common using monatomic water model, and the mW model of water does not have hydrogen atoms or electrostatics. Water molecules are represented as a single particle and able to form tetrahedral “hydrogen-bonded” structures through three-body nonbonded interactions. The interactions between mW water molecules consist of the sum of pairwise and three-body contributions described by the functional form of the Stillinger–Weber (SW) potential:

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\phi_2(r_{ij}) = A_{ij} \varepsilon_{ij} \left[ B_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left( \frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right)$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \varepsilon_{ijk} \left[ \cos \theta_{ijk} - \cos \theta_{0ijk} \right]^2 \exp \left( \frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left( \frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right)$$

where phi2 is a two-body term and phi3 is a three-body term. The summations in the equation are over all neighbor atoms of atom I within a cutoff distance. In our simulation, it just need to set up the  $\varepsilon = 6.189 \text{ kcal/mol}$ , and  $\sigma = 2.3925 \text{ \AA}$  to get mW water model.

LJ potential is described by following equation:  $E = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$ , and

specific parameters are listed in the Table. 1 in main text.

## Supplementary Note 2: Order parameters

In this simulation, order parameter  $q_6$  is used to distinguish liquid water and solid ice, and  $I_c$  and  $I_h$  is distinguished by order parameter  $q_3$ .<sup>3</sup>To calculate these order parameters, it need to calculate  $\bar{q}_{lm}(i)$  for each atoms firstly using following equation.

$$\bar{q}_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\theta(r_{ij}^{\mathbf{u}}), \phi(r_{ij}^{\mathbf{u}}))$$

where  $N_b(i)$  is the number of bonds for particle  $i$  defined within a cut-off radius of 3.2 Å,  $Y_{lm}$  is spherical harmonic,  $\theta$  and  $\phi$  denote the azimuthal and polar angles of orientation for bond  $r_{ij}^{\mathbf{u}}$ , respectively. Then order parameter  $q_l$  is calculated as following:

$$q_l = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} \frac{q_l^{\mathbf{r}}(i) \cdot q_l^{\mathbf{r}^*}(j)}{|q_l^{\mathbf{r}}(i)| |q_l^{\mathbf{r}^*}(j)|}$$

where  $q_l^{\mathbf{r}^*}(j)$  is the value of  $\bar{q}_{lm}$  for the each neighbor atoms of particle  $i$  defined within a cut-off radius of 3.2 Å. Specific criteria seeing in main text.

### Supplementary Note 3: Evidence of nanorods affecting the nucleus process

Comparing with the sphere of ice nucleus, ice nucleus with two-dimensional shape is easier to be influenced by nanorods, because it is earlier to expand to the influenced area by nanorods. To make our result be more convincing, we use mathematical calculations to further illustrate this question. We assume that 2nm is the critical nucleation size when ice nucleus is sphere shape. The volume of sphere with 2nm

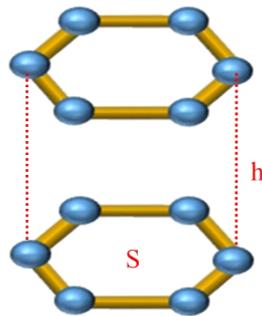
diameter is  $\frac{4}{3}\pi r^3 = 4.19nm^3$ . Furthermore, the ice nucleus is considered to be pure  $I_h$ ,

and the volume of single ice crystal cell can be calculated as  $V_0=Sh$ , as shown in Figure R1, where S is the bottom area and h is the height of ice crystal cell. In our simulation, the average distance between two water molecules is about 3 Å. S and h can be

calculated, and  $S = 6 \cdot \frac{\sqrt{3}}{4} l^2 = 0.2338nm^2$ , and  $h = 0.3nm$ . Therefore,  $V_0 = Sh = 0.07nm^3$  and the number of ice crystal cell in critical nucleus is about 60. If

the ice nucleus on plane is two-dimension shape, single ice crystal cell needs 0.2338nm<sup>2</sup> to spread. Also, 60 ice crystal cells need about 14nm<sup>2</sup>, and its radius is about 2.1nm, if the plane is a circle. It is clear that the plane between nanorods is too small (radius is about 1.5nm) for the formation of critical nucleus, and the nanorods affect the nucleation process indeed. On the other hand, it is hard to determine the length of the critical nucleus in Figure 3a, and we try to describe the size of critical nucleus using the number of water molecules instead of the length. It can be found that the structure of ice nucleus on 45°-inclination nanostructures begins to change in Figure 2g at 94.36ns, and the ice nucleus keeps in  $I_h$  on 90°-inclination structures, as shown in Figure 2c. We

make sure that the nanorods lead to this difference, and ice crystal is affected by nanorods at this moment. Through observation and detection, we find the ice crystal in Figure 2g contains 100-120 water molecules. In Figure 3a, when the number of freezing molecules begins to increase rapidly, the number of freezing molecules is about 150, which is larger than the size of nucleus in Figure 2g.



**Figure R1. The schematic diagram of single ice crystal cell.**

## References

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2. L. Lupi, A. Hudait, and V. Molinero, *Journal of the American Chemical Society*. 2014, **136**, 3156–3164
3. T. S. Li, D. Donadio, G. Russoc, G. Gallicd, *Phys. Chem. Chem. Phys.* 2011, **13**, 19807–19813.