Supporting Information

Metal-catechol complexes mediate the ice nucleation

Huige Yang,[a] Yunhe Diao,[a] Beili Huang,[a] Kaiyong Li*[b] and Jianjun Wang[c]*

Modifying the surfaces with metal-catechol complexes

For the preparation of the surfaces modified by metal-catechol complexes, a buffer solution of 10 mmol·L^{-1} containing *N*,*N*-bis(2-hydroxyethyl) glycine (bicine) was first prepared and its pH was adjusted to 8.5 by ammonia solution. Then, the cleaned silicon wafers were immersed into a solution of 3,4-dihydroxyphenylalanine (DOPA) (2 mg·mL^{-1}), which was prepared by dissolving DOPA in a bicine buffer solution, for 24 h at the room temperature. The DOPA-functionalized surfaces were placed in a vial of 50 mL ultrapure water (18.2 MΩ·cm) for 10 minutes, and afterwards the samples were blown dry by a stream of high purity argon. Thereafter the DOPA-functionalized surfaces were immersed into a solution of targeted metal ions (0.1 mol·L^{-1}, prepared by dissolving $AgNO_3$, $CoCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $ZnCl_2$, $AlCl_3$, $FeCl_3·6H_2O$ in ultrapure water) for 24 h at the room temperature. Finally, the surfaces modified by metal-catechol complexes were placed in a vial of 50 mL ultrapure water for 10 minutes, and was blown dry by a stream of high purity argon. The whole process of sample preparation was carried out in a Class II Type A2 bio-safety cabinet, in which the number of airborne particles was equivalent to that of a “Class 100” clean room.

Surface characterization and the verification of surface modification with DOPA and metal-catechol complexes

The static contact angles (CAs) on the samples were measured at the room temperature with CA System (DSA100, Krüss Co., Germany). The topographical images and roughnesses of the surfaces were acquired by using atomic force microscopy (AFM) (Multimode8, Bruker Nano Inc., Germany) in the ScanAsyst mode. The surface chemistry composition was measured by X-ray photoelectron spectroscopy (XPS, ESCALab220i-XL).

Table S1. The contact angles of the surfaces modified by DOPA and a variety of metal-catechol complexes.

Samples	Contact angle (°)
silicon wafer	49.0 ± 2.4
DOPA-functionalized surface	38.8 ± 1.4
Ag(I)-chelated surface	39.6 ± 3.4
Ca(II)-chelated surface	23.7 ± 2.1
Cu(II)-chelated surface	47.7 ± 5.0
Co(II)-chelated surface	47.1 ± 3.1
Zn(II)-chelated surface	45.3 ± 2.6
Fe(III)-chelated surface	39.3 ± 2.1

Al(III)-chelated surface	92.7 ± 3.4

Table S2. The values of average surface roughness, R_a, of the surfaces modified by DOPA and a series of metal-catechol complexes.

Samples	R_a (nm)
silicon wafer	0.53 ± 0.14
DOPA-functionalized surface	1.43 ± 0.24
Ag(I)-chelated surface	1.24 ± 0.16
Ca(II)-chelated surface	1.33 ± 0.39
Cu(II)-chelated surface	2.18 ± 0.59
Co(II)-chelated surface	2.46 ± 0.35
Zn(II)-chelated surface	1.99 ± 0.24
Fe(III)-chelated surface	1.29 ± 0.09
Al(III)-chelated surface	2.84 ± 0.05

Measurement of quartz crystal microbalance with dissipation (QCM-D)

First, the chip of QCM-D was immersed into DOPA solution (2 mg·mL^{-1}) for 24 h at the room temperature. After being rinsed by ultrapure water and blown dry by a stream of high purity argon, the DOPA-functionalized surfaces were immersed into a solution of targeted metal ions (0.1 mol·L^{-1}, prepared by dissolving $FeCl_3 \cdot 6H_2O$ in ultrapure water) for 24 h at the room temperature. Finally, the surfaces modified by Fe^{3+}-catechol complexes were rinsed by ultrapure water and blown dry by a stream of high purity argon.

The quartz crystal microbalance with dissipation (QCM-D) was employed for investigating the variation in the frequency and dissipation. Figure S1 shows that there is no variation in the frequency and dissipation, demonstrating that the dissociations of DOPA and metal-catechol complexes do not occur and they remain stable upon contact with water.

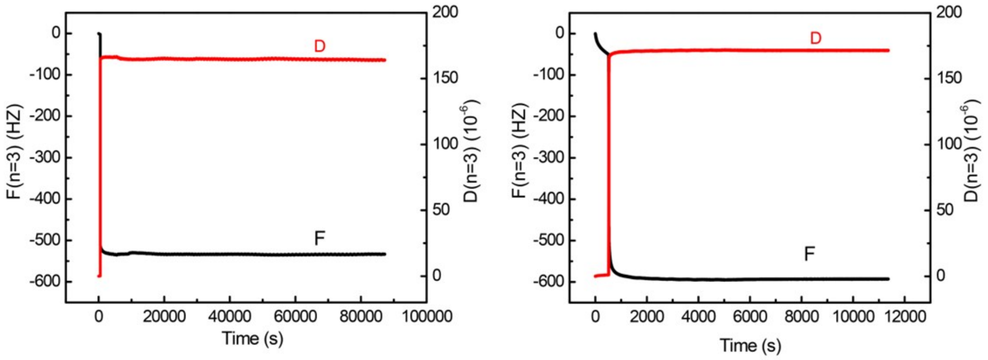

Fig.S1 The changes in QCM-D resonant frequency and dissipation as a function of time for the DOPA-functionalized surface (a) and the surface modified by Fe^{3+}-catechol complexes (b) immersed in ultrapure water.

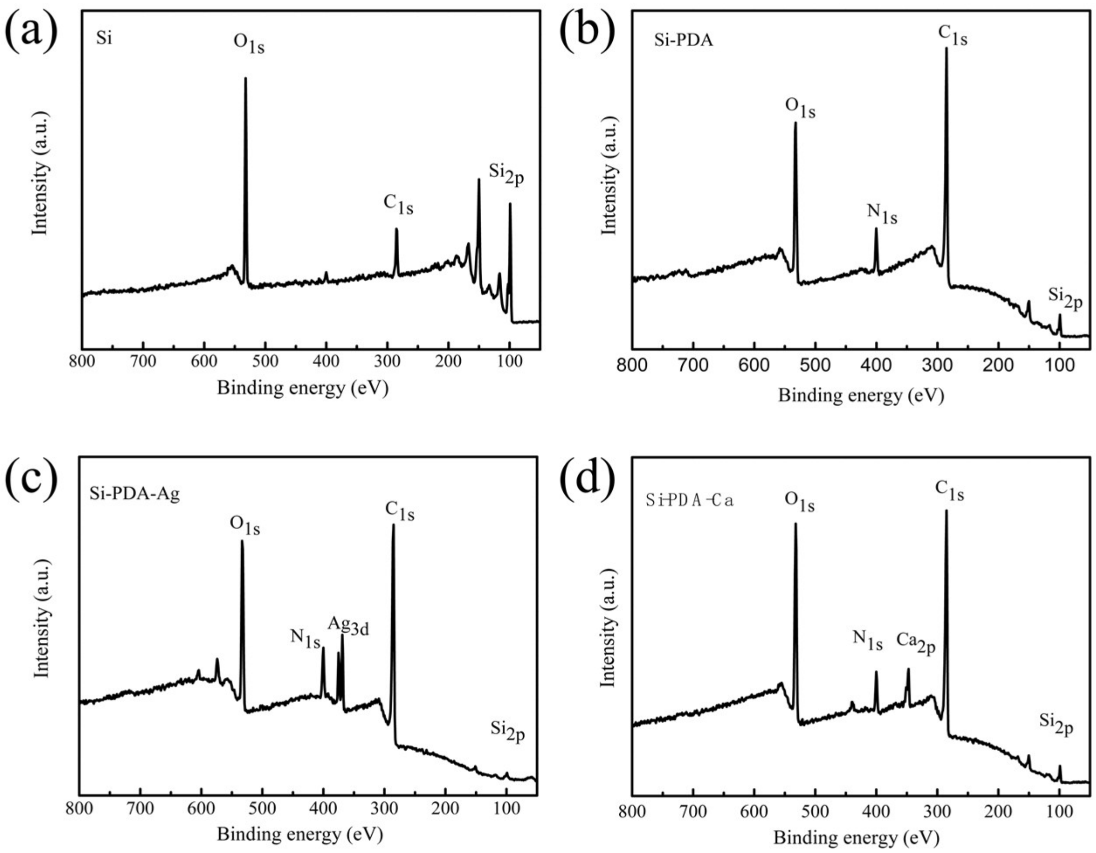

Fig.S2 The XPS survey scans of the pristine silicon wafer (a), the DOPA-functionalized surface (b), the surfaces chelated with Ag^+ (c) and Ca^{2+} (d).

Measurements of the temperatures and delay times of ice nucleation of water macrodroplets on the surfaces

The measurement of ice nucleation temperatures of water macrodroplets deposited directly on the surfaces modified by metal-catechol complexes was carried out in a home-built cell. The procedure for the deposition of water macrodroplets and the fabrication of sample cell was conducted in a bio-safety cabinet. Specially, three to four macrodroplets of 0.1 μL ultrapure water were separately placed atop the substrate to be tested to ensure that individual macrodroplet froze independently without triggering/affecting the freezing of the proximal ones. Then, the surface was cooled at different rates, namely, 2, 5, 10 and 15 ^{o}C·min^{-1} to induce the occurrence of ice nucleation and the temperatures of ice nucleation were recorded. The freezing tests were repeated 50-60 times to produce a reliable statistics of the ice nucleation temperature.

Similarly, the measurement of delay time of ice nucleation was also conducted in a home-built cell to ensure that the experiments were carried out in a closed environment of constant relative humidity of 100%. A macrodroplet of 0.1 μL ultrapure water was placed atop the substrate to be tested. The procedure for the deposition of water macrodroplets and the fabrication of sample cell were also conducted in a bio-safety cabinet. The surface was cooled to a targeted temperature of -17.0 ^{o}C and then held constantly until the macrodroplet completely froze. The moment when the surface temperature reached -17.0 ^{o}C is referred to as the starting time, and the difference between the starting time and the time taken by the droplet for ice nucleation to occur is defined to be the delay time of ice nucleation.

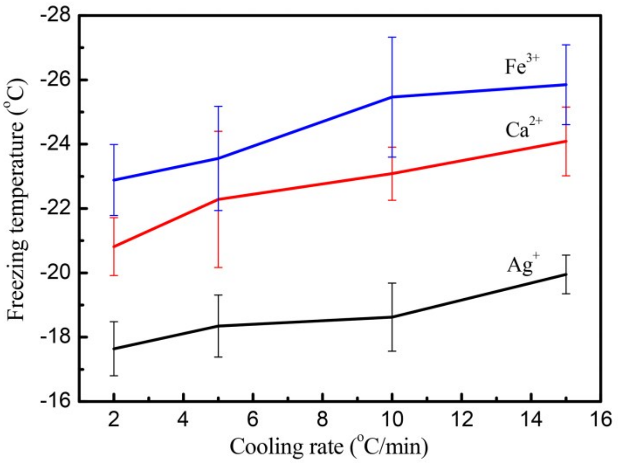

Fig.S3 The dependence of ice nucleation temperature on the cooling rate on the surfaces chelated with Ag^{+}, Ca^{2+} and Fe^{3+}.

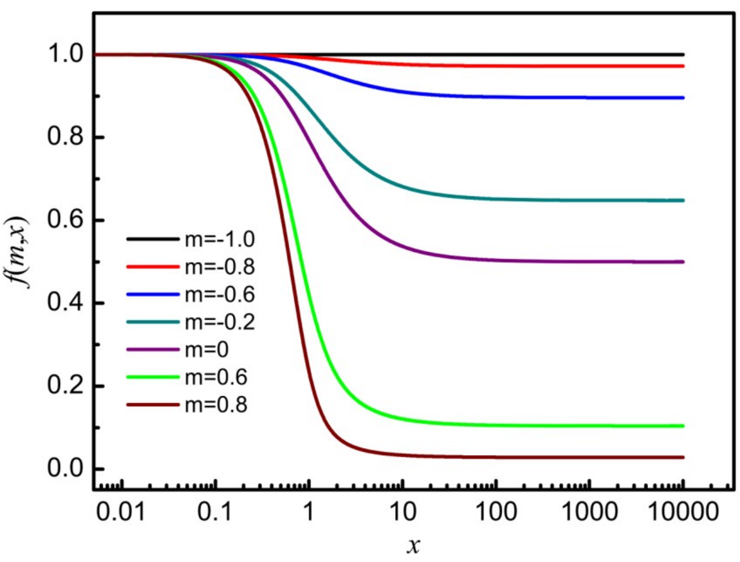

Fig. S4 The function of geometrical factor for heterogeneous ice nucleation, $f(m,x)$, is plotted in terms of the ratio x, and m is shown as a parameter.