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Tuning Solid Surfaces from Hydrophobic to Superhydrophilic by Submonolayer Surface Modification

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Molecular-scale understanding and manipulation of the wetting behavior of water on solids remains a fundamental challenge. Using diamond as a model system, we show that the naturally hydrophobic behavior of a hydrogen-terminated C(111) surface can be manipulated by replacing the H termination with a monolayer of adsorbate. In particular, a mixed monolayer of $\frac{1}{3}$ Na and $\frac{2}{3}$ F atoms leads to superhydrophilic behavior, as shown by first-principles calculations. The physical origin of the superhydrophilic behavior is attributed to the ionic nature of the Na adatoms, which mediate the *right* degree of binding strength between water molecules and the substrate.

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A microscopic understanding of the wettability of solid surfaces is fundamentally intriguing and practically important [1,2]. The extreme limits, defined by the water-surface contact angle θ_c , with $\theta_c > 130^\circ$ and $\theta_c < 5^\circ$ for superhydrophobic and superhydrophilic behavior, respectively, are immensely useful in industrial applications such as antifogging and self-cleaning [3–7]. In particular, superhydrophilic behavior is desirable in a wide range of biomedical applications, protecting biomolecules from damage in their interaction with biomaterials.

Several empirical, conceptually different methods have been developed to achieve superhydrophobicity, including chemical modification or mechanical stretching of the interfaces, and controlled surface roughness (the “lotus effect”) [3,4]. Attempts have also been made to tune the wettability of a given surface from hydrophobic to hydrophilic, including ultraviolet irradiation [5,6] of TiO₂ and ZnO, thermal treatment [7] of Al₂O₃, and coating of Au and Ag substrates with self-assembled organic monolayers [8]. These methods are not readily applicable to, or stable in, a biomedical environment. Manipulating the hydrophobic or hydrophilic behavior at will would be very desirable. Currently, this is not feasible because the principles that determine the macroscopic scale wetting behavior and their relation to the microscopic atomic-scale features have not yet been elucidated.

In this Letter, we propose a new approach to tune the wettability of solid surfaces. We show through first-principles simulations that by carefully chosen modifications of the surface structure at the submonolayer level, a model system—diamond (111)—can be tuned from highly hydrophobic to superhydrophilic. Although demonstrated on diamond, the general principles of our approach should be applicable to other similar situations.

As a first step, we identify three general factors that are critical in determining optimal water-surface contact:

- (i) The water-surface binding strength has to be strong, but without leading to dissociation of the water molecule.
 - (ii) The molecular orientation of an isolated H₂O molecule upon adsorption should favor subsequent ice nucleation.
 - (iii) In order to grow a stable film of significant thickness, the ice-substrate lattice mismatch should be minimal.
- From (iii), it is evident that one must start with a substrate that has the right crystal structure and lattice constant. However, it is shown repeatedly [9] that minimizing the lattice mismatch alone is insufficient in achieving extreme hydrophilicity or even improved wettability.

We consider diamond as a model system because it has many advantages. First, diamond offers an easy way to satisfy the third requirement, because its (111) surface with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ (RT3) periodicity is a hexagonal lattice with a lattice constant (4.37 Å) very close to that of the naturally occurring ice Ih (4.48 Å, a mismatch of ~2%). In addition to generally useful properties such as transparency, extreme hardness, high thermal conductivity, and high resistivity, diamond is also known to be a biocompatible material and binds biomolecules strongly [10], which allows for interesting biomedical applications. Finally, recent breakthroughs have made diamond economically accessible [10].

The natural surface of diamond, the C(111) surface fully passivated by hydrogen, is known to have negligible attraction to water molecules despite the nearly perfect lattice match [11]; therefore, such a surface exhibits extreme hydrophobic behavior. To modify this behavior, we consider adsorbates that will preserve the surface passivation but have different affinity for water. We replace $\frac{1}{3}$ monolayer (ML) of by alkali metals (A) ordered in the RT3 structure, while the remaining surface C sites are saturated by either H or other elements or groups of atoms (generically referred to as X, Fig. 1); examples include F, Cl, and methyl (CH₃). The resulting systems are denoted as

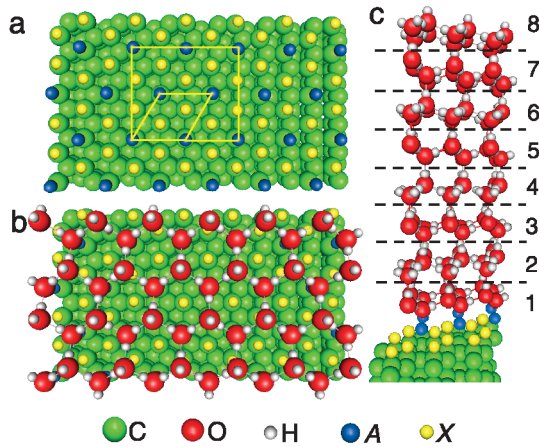


FIG. 1 (color). Geometry of the diamond-ice contact. (a) Top view of the modified C(111) surface, terminated by $\frac{1}{3}$ ML of alkali metal atoms (A) and $\frac{2}{3}$ ML of X elements in an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice. Supercells used in the calculation are indicated by yellow lines. (b) Top view of the first water bilayer adsorption on this surface. (c) Side view of eight water bilayers on the surface.

C(111)-(A, X) hereafter. This strategy is naturally appealing and promising for the following reasons: First, the surface dangling bonds of the C atoms have to be saturated by either H or the new element in order to form a stable surface for realistic applications; alkali metals, halogens, and methyl groups, just like H, serve this purpose perfectly. Second, alkali metal *ions* are known to bind strongly to, but do not dissociate, water molecules. Third, most alkali elements, especially K and Na, and many halogens are naturally present in biological environments as in the human body.

To evaluate the proposed surface modifications, we employ first-principles calculations in the framework of density-functional theory, a well-established methodology with predictive powers. For the calculations we use VASP [12] with projector-augmented-wave pseudopotentials [13] and the Perdew-Burke-Ernzerhof functional [14], which are the most reliable in describing the hydrogen bonds and bulk properties of water [15], as well as surface properties. We model the surface by a supercell slab geometry [16].

We address first the (super)hydrophobic nature of the H-passivated C(111) surface. To this end, we have calculated the adsorption energy on this surface and find it to be 26 meV for a single water molecule. The potential energy as a function of water-surface distance and orientation is shown in Fig. 2. Because the lattice constant of the C(111) surface matches that of the (0001) surface of ice Ih with minimal strain, water in principle could also form ice overlayers on C(111)-H. Such ice overlayers are similar in structure to bulk ice, whose elemental building block is a bilayer [17, 18]. Within a water bilayer, the molecules form a puckered hexagonal network, and there are two molecules per unit cell, connected by hydrogen bonds, with a

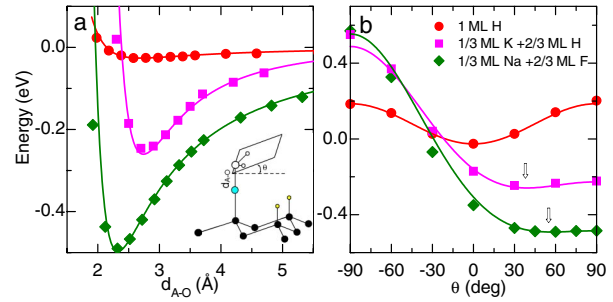


FIG. 2 (color online). Calculated energy dependence of water adsorption on: (a) the distance between A and O (d_{AO}); (b) the angle between the water molecule and the surface plane (θ , see inset). Curves are fitted according to Eq. (1).

difference of 0.96 \AA in their positions in the (0001) direction. We have also calculated the bilayer adsorption energy of water on C(111)-H and found it to be $435 \text{ meV}/\text{H}_2\text{O}$. This value is much smaller than the ice formation energy $E_{\text{ice}} = 670 \text{ meV}/\text{H}_2\text{O}$ (our result, which agrees well with Refs. [2, 15]). As a rough estimate, we can use the linear relationship between contact angle and monomer adsorption energy established for water adsorption on graphite [19] to obtain the contact angle of water on C(111)-H: we find this to be 145° , illustrating the superhydrophobic nature of this surface. Indeed, experiments [11] show that *diamondlike* films are hydrophobic, with $\theta_c \approx 100^\circ$.

We next examine the adsorption of water onto the C(111)-(A, H) surfaces by first considering $A = \text{K}$ and Na . Detailed calculations show that both K and Na are partially ionized upon adsorption due to net charge transfer from the alkali adatoms to the C atoms. The ionized nature of the adsorption, in turn, enhances the binding strength of the water molecule, which is equal to 246 and 345 meV on C(111)-(K, H) and C(111)-(Na, H), respectively. Although both values are much higher than 26 meV on C(111)-H, they are still not strong enough to induce wetting, because the bilayer adsorption energies of water on C(111)-(K, H) and C(111)-(Na, H) are, respectively, only 511 and 568 meV per H_2O , still significantly lower than E_{ice} .

Remarkable improvements in wettability are achieved by terminating other C sites with F in a structure we refer to as C(111)-(Na, F). For this surface, we considered water interaction at three levels: single water adsorption, bilayer ice formation, and multilayer ice growth. For the single water molecule, we find an adsorption energy of 490 meV, much higher than the cases of C(111)-(K, H) and -(Na, H) [see Fig. 2(a)]. The molecular geometry is very similar, but the C-Na (2.38 \AA) and Na-O (2.32 \AA) bond lengths are both shorter than the corresponding bond lengths on C(111)-(Na, H) (2.50 and 2.38 \AA).

For ice bilayer formation, the spatial orientation of a single molecule comes into play. We find the angle between the water plane and the C(111)-(K, H), -(Na, H) surfaces to be $\theta \sim 40^\circ$ [Fig. 2(b)], very close to $\theta_0 = 36^\circ$, the corresponding value in bulk ice. On

C(111)-(Na, F) this angle increases to $\theta = 56^\circ$, still close to the ideal angle. The energy dependence on water adsorption height and orientation in Fig. 2 can be fitted by a simple formula with electrostatic, Lennard-Jones, and angle-dependent interactions:

$$U(d, \theta) = \frac{q_A q_H}{d_{AH}} + \frac{q_A q_O}{d} + \frac{A}{d^{12}} - \frac{C}{d^6} + \frac{a - b \cos 2\theta}{d}, \quad (1)$$

where d is the distance between A and O; d_{AH} (the distance between A and H) is determined by d , θ , and the water molecule geometry from the TIP3P water model [20]. We also use TIP3P point charges, $q_H = 0.417e$ and $q_O = -0.834e$. Other parameters are listed in Table I.

More critically, an isolated ad-water is free to rotate along the azimuthal angle with a negligible energy barrier calculated to be 3 meV. Therefore, the ad-water is ideally oriented to serve as a nucleation center for bilayer formation. Indeed, the adsorption energy of an ice bilayer on C(111)-(Na, F) is 674 meV per H₂O. This affinity is slightly higher than E_{ice} , leading to the formation of a perfect two-dimensional water layer on the C(111)-(Na, F) surface, that is, superhydrophilic.

Beyond the bilayer thickness, lattice mismatch become increasingly important in defining the critical thickness, above which water droplets become more favorable than 2D bilayers. Since C(111)-(F, Na) is almost perfectly matched to ice lattice, the adsorption energy per H₂O is always larger or comparable to E_{ice} as the total number of bilayers increases, shown in Fig. 3. Water wets C(111)-(Na, F) with at least eight bilayers, thereby inducing superhydrophilic behavior to the system, with $\theta_c = 0$ defined at the molecular level. Considering this as the limit at which the substrate starts to develop zero contact angle, and assuming a linear relationship between contact angle and monomer adsorption energy, $\theta_c = (1 - E_{ads}/0.49 \text{ eV}) \times 180^\circ$ [21], we determine *approximate* values of $\theta_c = 53^\circ, 90^\circ$, and 170° for C(111)-(Na, H), -(K, H), and -H, respectively; a nonlinear dependence of θ_c on adsorption energy [22] may lead to different values without affecting the qualitative conclusions.

For comparison, we also plotted the thickness dependence of bilayer adsorption energy on other C(111)-(A, X) surfaces, and generally wetting metal substrates, such as Pt(111) [23], shown in Fig. 3. All the results are qualitatively different from the C(111)-(Na, F) case. The adsorp-

tion energies for these C(111) systems are consistently lower than E_{ice} . We note that for each case on C(111), the adsorption energy does approach E_{ice} at higher film thicknesses, a reflection of the minimal strain between the water overlayer and the substrate.

The C(111)-(Na, F) system is the only case in which adsorption energies of a molecular water bilayer and subsequent multilayers are higher than the ice formation energy. All other studies in which water adsorbs on different substrates *as intact molecules* give much lower adsorption energies (450–550 meV). Examples include water adsorption on noble metals, salts, mica [24,25], and the other C(111)-(A, X) systems considered here [except for C(111)-(Li, CH₃, H), which has a more delicate structure]. In fact, even the half-dissociated water layer on Ru(0001) [2], with an adsorption energy of 660 meV, is still less stable. Only highly reactive metal surfaces [25], such as Fe or Ti, and oxide surfaces [26], such as TiO₂, may have larger water adsorption energies ($\sim 1 \text{ eV}/\text{H}_2\text{O}$ for the first layer), but water adsorption is typically dissociative on such surfaces, making the formation of multilayer films less likely.

An important consideration is the feasibility of preparing the proposed C(111) substrates experimentally. First, F has an adsorption energy of 5.13 eV on C(111), stabilizing the sp^3 hybridization of surface C atoms. Initially, about $\frac{1}{3}$ ML of the F atoms on F-terminated C(111) can be removed by laser or heat desorption. Then, roughly $\frac{1}{3}$ ML of Na atoms can be deposited, which will saturate the dangling bonds exposed after partial F desorption, leaving a surface terminated with $\frac{2}{3}$ ML F plus $\frac{1}{3}$ ML Na atoms. The driving force for the originally randomly distributed $\frac{1}{3}$ ML of Na atoms to self-organize into an ordered RT3 superstructure is the dipolelike interaction among the Na and F adatoms. Our density-functional theory calculations show that the Na-Na and F-F interactions are both repul-

TABLE I. Parameters in Eq. (1) fitted to the calculated data.

	q_A (e)	A ($10^3 \text{ eV} \cdot \text{\AA}^{12}$)	C ($\text{eV} \cdot \text{\AA}^6$)	a ($\text{eV} \cdot \text{\AA}$)	b ($\text{eV} \cdot \text{\AA}$)
C(111)-H	0	24.477 ^a	0.253 ^a	0.286	0.286
C(111)-(K, H)	0.40	24.767	83.275	0.230	0.250
C(111)-(Na, F)	0.47	3.196	13.848	-0.189	0.243

^aFor C(111)-H, we use an 8-2 potential, with A in $\text{eV} \cdot \text{\AA}^8$ and C in $\text{eV} \cdot \text{\AA}^2$.

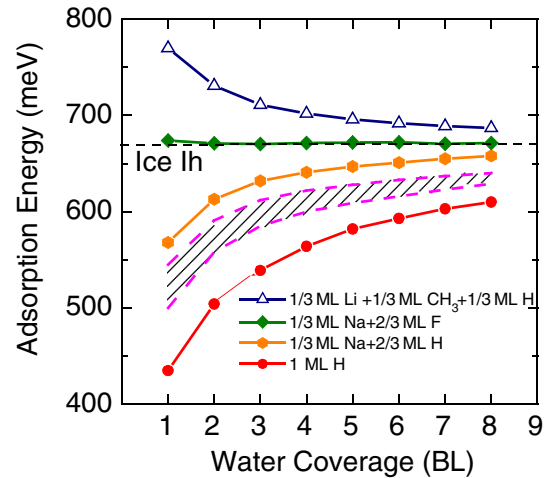


FIG. 3 (color online). Adsorption energies for up to eight water bilayers (BL). Shaded region shows schematically results for other modified C(111) surfaces and Pt(111) [23].

sive, with strengths of 773 and 82 meV on nearest-neighbor sites, respectively. In contrast, the Na-F interaction is attractive, -204 meV. With these interactions, our Monte Carlo simulations at 310 and 1000 K allowing site exchange between Na and F show that an initially randomly distributed $\frac{1}{3}$ ML of Na and $\frac{2}{3}$ ML of F atoms easily self-organize into the RT3 structure.

Possible reactions of water with the substrate may also occur. It is known that *t*-butyl-A ($A = \text{Li, Na, K}$) molecules, which resemble the local structure of an A atom on the C(111) surface, react strongly with water exchanging A with H. However, on C(111)-(Na, F) this reaction is inhibited by the presence of a large barrier, 0.7 eV for single water adsorption and 1.4 eV in the bilayer. This comes from the strong repulsion when Na approaches F, blocking the active C sites from being exposed to water. Moreover, the reaction $\text{C}-\text{Na} + \text{H}_2\text{O} \rightarrow \text{C}-\text{H} + \text{NaOH}$, where C—stands for a C surface site on C(111), is endothermic by 0.5 eV. Therefore it is safe to deposit water molecules at least at the low temperature of ~ 230 K and then form bilayers that are stable up to room temperature and higher. Indeed, we have found that in molecular dynamics simulations lasting for 3 ps, the water bilayer on C(111)-(Na, F) preserves the intact ice structure even at 320 K, without reaction or even melting.

The following question arises: What is the physical origin of the superhydrophilic behavior of C(111)-(Na, F)? It is known that a Na^+ ion in free space binds water molecules strongly with an energy of 1.1 eV [27]. To address the question, we search for similar behavior in the C(111)-(Na, F) system by examining charge density differences $\Delta\rho$, defined as the difference between the total charge and that of separated subsystems. The calculated $\Delta\rho$ for the free Na^+ -water system indicates a strong polarization of the water molecule induced by the free Na ion, which is responsible for the strong binding. The polar character of Na-water binding is well preserved on C(111)-(Na, F). The strong binding and tunability between alkali ions and water can therefore be attributed to the partially ionized nature of the alkali atoms on the C(111) surface. Our electron density analysis shows that, upon adsorption, each Na adatom develops a net charge of about $+0.40e$ on C(111)-(Na, H) and $+0.45e$ on C(111)-(Na, F), consistent with the parameters fitted in Eq. (1). Such a partially ionized Na forms relatively strong electrostatic Na-O bond with water, with energies of 0.35 and 0.49 eV for C(111)-(Na, H) and -(Na, F), respectively, though both values are significantly lower than the value for the Na^+ -water bond (1.1 eV). In the case of C(111)-(Na, F), the neighboring F ionizes Na further, resulting in the enhanced binding energy of a water bilayer which exceeds E_{ice} and the consequent superhydrophilic behavior.

Besides stability and biocompatibility, another unique advantage of our method is that it relies on the ionic nature of the surface-water interaction; this is useful for exploring the role of electrostatic interactions, counterions, and

added salt in wetting by aqueous solvents [28], which could be especially important for biomedical application. The tunable surface-water interaction achieved by partial ionization of adatoms can be instrumental in the design of other similar materials with desirable wetting properties.

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