

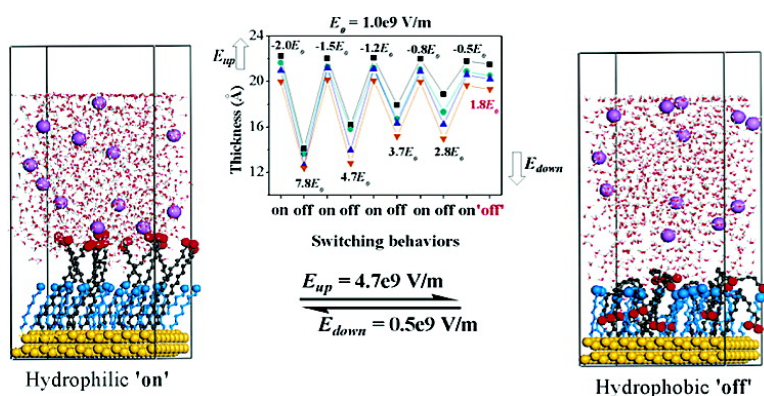
Article

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Electric Field Induced Switching Behaviors of Monolayer-Modified Silicon Surfaces: Surface Designs and Molecular Dynamics Simulations

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Abstract: Electric field induced switching behaviors of a series of low-density ω -carboxyalkyl modified H-Si(111) and the mixed ω -carboxyalkyl/alkyl covered H-Si(111) have been simulated by using molecular dynamics (MD) simulation techniques. The external electric fields may drive surface-confined molecules to reversibly change conformations between the all-trans (switching 'on') and the mixed trans-gauche (switching 'off') states. Such surfaces switch wettabilities between the hydrophilic state and the moderately hydrophobic state. It has been found in broad ranges of intensities of applied electric fields, -2.0×10^9 V/m $\leq E_{\text{down}} \leq 0$ and 1.8×10^9 V/m $\leq E_{\text{up}} \leq 7.3 \times 10^9$ V/m, both the low-density (11.1%–33.3%) ω -carboxyalkyl and the mixed ω -carboxyalkyl/alkyl (in mole fraction of $0.4 \leq N_{\text{carboxyalkyl}} : N_{\text{alkyl}} \leq 3.0$) monolayers covering H-Si(111) exhibit conformational switching in the aqueous medium. The *critical intensity* of the electric field, $E_{\text{up}} = 1.8 \times 10^9$ V/m, which is required to trigger the switches is observed by our MD simulations and further rationalized by a thermodynamical model. Some important factors in the control of switching performances, such as the steric hindrances, the formation of the electric double layer at the monolayer/electrolyte solution interface, the hydration effects of carboxylate anions, the components of surrounding electrolyte solutions, as well as the rigidity of surface-confined chains are elucidated. The lower ionic strength and additions of acetonitrile molecules in the surrounding aqueous solution can reduce the value of *critical intensity* of the electric field and hence facilitate the realization of switching. Some practical considerations in construction and optimum design of switching surfaces are also suggested.

1. Introduction

The technology of the modification of solid surfaces, such as gold and silicon surfaces with organic molecules or polymers, offers a wealth of opportunities for us to design 'smart' surfaces, which are responsive to different stimuli.^{1,2} By adjusting molecular structures and compositions of surface-covered molecules, many interesting surfaces with unique properties in response to the external stimuli such as electric potential,^{3–6} temperature,^{7,8} pH alternation,⁹ and light,^{10,11} and so forth are realized. These 'smart' surfaces are anticipated to be applicable in many fields such as the development of drug delivery systems, data storage devices, and microelectronic applications, and so forth.

Recently, a novel design of the switching surface that enables surface wettability to reversibly switch between the hydrophilic state and the hydrophobic state in response to the external electric potential is demonstrated with a low-density, carboxylic acid ended monolayer modified Au surface.³ This type of surface design enables the amplification of conformational transitions at the molecular level to macroscopic changes in surface properties with the systems' environment unaltered, stimulating our designs of new surface apparatuses.

We attempt to theoretically explore some other monolayer-modified surfaces, which may also exhibit interesting switching behaviors such as those reported on Au surfaces³ under the external stimuli. The single-crystal silicon surfaces present possible candidates in this kind of surface design for their fascinating electric properties and reactivity with various organic reagents.^{12–14} Traditionally, modifications of silicon surfaces with organic monolayers were mainly achieved via the use of the siloxane chemistry with the presence of an insulating oxide

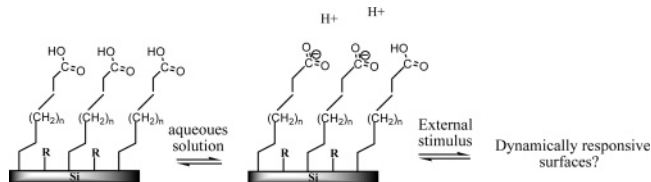
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interlayer, which may not be desirable in some applications.^{12–14} Chidsey et al. made pioneering work in preparing covalently attached organic monolayer modified silicon surfaces from the hydrogen-terminated Si(111) and Si(100) surfaces.¹⁵ Until now, it has been possible to prepare the monolayers modified silicon surfaces from the thermal,^{16–22} catalyzed,^{23–25} radical-initiation,^{26,27} or photochemical reactions^{28–30} of hydrogen-terminated or halogenated terminated Si(111) or Si(100) with alkenes, Grignard reagents, or aldehydes and by the electrochemical reduction of aryldiazonium ions. Similar reactions were also reported for the modifications of the porous silicon.^{31–34} In many of these modification procedures, the resultant organic films on silicon surfaces are terminated with methyl groups and have substituted chains densely packed. However, the low reactivity of terminated methyl groups and densely packed structures of monolayers restrict the further manipulation of chemical and physical properties of surfaces. The possibility of creating functionalized organic film-modified silicon surfaces has been explored by some groups.^{17,35–42} So far, some functional groups (such as the carboxylic acid,^{17,38–40} the ester,⁴¹ and the amino⁴²) terminated organic films modified silicon surfaces were prepared, which represent advances in our ability to manipulate the chemical and physical properties of surfaces. Now, they offer a chance for us to construct the novel dynamically responsive silicon surfaces.

We start our theoretical designs of switching surfaces from the reported carboxylic acid (–COOH) terminated monolayers

Scheme 1. Can We Construct Some Dynamically Responsive Surfaces Based on These Dissociated Carboxylic Acid-terminated Monolayers?



R = H or short alkyl chains

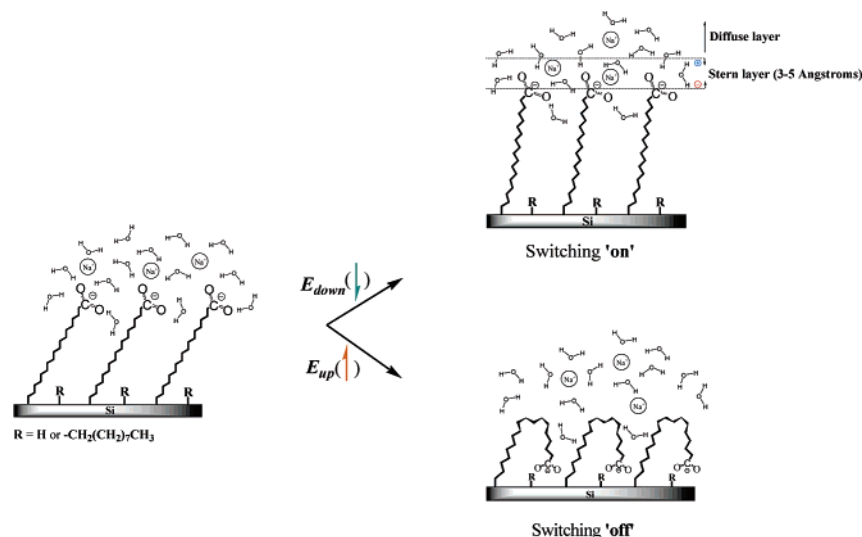
modified silicon surfaces. Surfaces covalently attached by carboxylic acid-terminated monolayers have traditionally been created by oxidizing polymer surfaces,⁴³ functionalizing alkyl-siloxane monolayers formed on hydroxylated silicon substrates,⁴⁴ or adsorbing –COOH-terminated organosulfur molecules on gold.⁴⁵ The preparation of the densely packed ω -carboxyalkyl monolayer-modified H-terminated silicon surfaces was first contributed by Sieval et al. via thermal hydrosilylation of the H–Si(100) with ester-terminated 1-alkenes and further hydrolysis.¹⁷ Improved procedures of preparations of carboxylic acid-terminated monolayers modified H-terminated silicon surfaces were reported in recent years.^{35–38} In addition, the mixed ω -carboxyalkyl/alkyl modified H-terminated silicon surfaces were also reported.⁴⁰ Depending on the pH value of the supporting aqueous solution, the acidic properties of carboxylic acid functionalized surface-confined molecules are significantly different from those in bulk aqueous solutions. The reported protonation and deprotonation of acid-bearing monolayer typically occur in a broader range of pH values.^{39,40,43,46,47} In these systems, as shown in Scheme 1, the terminated carboxylic acid groups significantly ionized into carboxylate anions (–COO[–]), which make monolayers be terminated with the negatively charged carboxylate groups. Then, can we construct some dynamically responsive switching surfaces by introducing the external stimuli?

In the present work, we demonstrate surface designs and atomic molecular dynamics (MD) simulations on the dynamical switching, ‘on’ and ‘off’ (cf. Scheme 2), of the low-density –COOH-terminated monolayers modified H–Si(111) driven by external electric fields. Another MD simulation study (without the explicit descriptions of solvent molecules and Au surfaces) on the electric field induced switching of poly(ethane glycol) terminated monolayers was just reported when we are going to submit our revised manuscript.⁴⁸ Two series of surface models

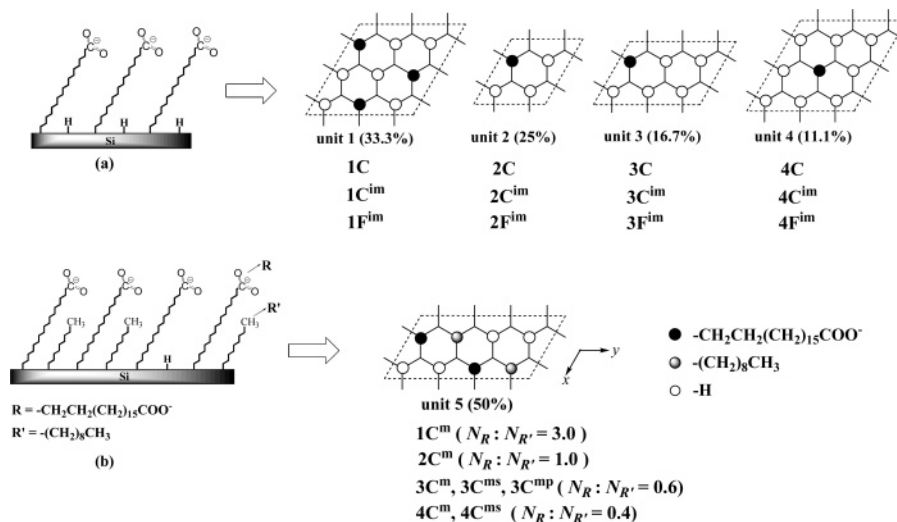
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Scheme 2. Switching Behaviors, 'on' and 'off'



Scheme 3. Two Series of Monolayers Modified H–Si(111) (cf. Table 1 in detail)



based on the H-terminated Si(111) are theoretically designed in our simulations with the supporting electrolyte solution is mimicked by both explicit and implicit solvent models. One series of surfaces is the low-density ω -carboxyalkyl monolayers modified H–Si(111), such as **1C–4C**, **1C^{im}–4C^{im}**, and **1F^{im}–4F^{im}** as shown in Scheme 3(a), which are substituted by evenly distributed $-(\text{CH}_2)_{17}\text{COOH}$ (or partially fluorinated $-(\text{CH}_2)\text{CH}_2(\text{CF}_2)_{15}\text{COOH}$) chains with coverage ranging from 11.1% to 33.3%. While another series, **1C^m–4C^m**, **3C^{ms}–4C^{ms}**, and **3C^{mp}** as shown in Scheme 3 (b), have the H–Si(111) modified by the zigzag pattern, $\sim 50\%$ coverage, mixture of $-(\text{CH}_2)_{17}\text{COOH}$ and $-(\text{CH}_2)_8\text{CH}_3$ chains in different molar fractions ($0.4 \leq N_{-(\text{CH}_2)_{17}\text{COOH}} : N_{-(\text{CH}_2)_8\text{CH}_3} \leq 3.0$). By using molecular dynamics simulations, we systematically investigate the molecule-level information on the reversible switching of both low-density ω -carboxyalkyl covered and the mixed ω -carboxyalkyl/alkyl monolayers modified H–Si(111) under wide ranges of intensities of external electric fields, $-2.0 \times 10^9 \text{ V/m} \leq E_{\text{up}} \leq 0$ and $1.8 \times 10^9 \text{ V/m} \leq E_{\text{down}} \leq 7.3 \times 10^9 \text{ V/m}$, by assuming the terminated $-\text{COOH}$ groups are significantly deprotonated in supporting electrolyte solutions. During the switching processes driven by electric fields, some intrinsic effects including the steric hindrances of neighboring surface-confined chains and

solvents, the hydration effect of carboxylate anions, as well as formations of interfacial electric double layers at the monolayers/ aqueous solution interfaces appearing, which influence switching performances of surfaces greatly and further directly determine the value of the *critical intensity* of the electric field that needed to trigger the switch. Beyond these intrinsic effects, some tunable factors such as the rigidity of surface-confined chains and the component of supporting electrolyte solutions are also theoretically explored in our simulations by introducing the $-\text{CF}_2-$ groups into the surface-confined chains (**1F^{im}–4F^{im}**) and by adding acetonitrile molecules into the surrounding aqueous solutions (**3C^{ms}–4C^{ms}**), which provide comprehensive insights into switching phenomena of this kind of monolayer-modified surfaces and guide the optimization of surface designs. It is anticipated that our simulation results on various surface models provide useful information to design some new functional surfaces, since the results can be extended to other switching surfaces without the loss of generality.

2. Computational Models and Details

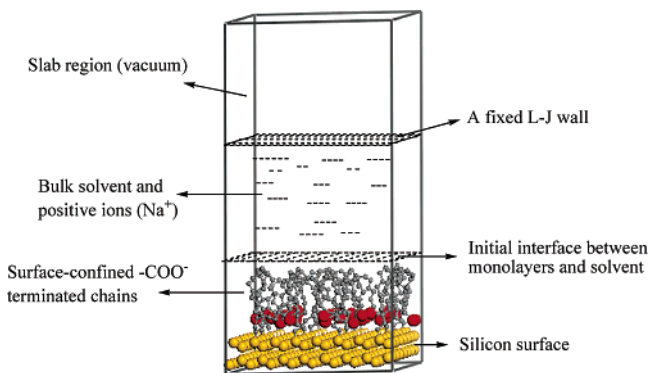
2.1. Surface Models. To realize switching processes of these $-\text{COOH}$ -terminated alkyl monolayers modified H–Si(111), an important factor of the conformational freedom available for transitions

Table 1. Selected Surface Models

models	surface chains ^a	solvent molecules ^a	ions (Na ⁺) ^a	area per -COOH-terminated chains (Å ² /chain)	cell parameters ^b (x,y)
explicit solvent models (aqueous solution)					
1C	27 (-RCOO ⁻) ^c	1315(w)	27	38.3	34.56, 34.56
2C	16 (-RCOO ⁻) ^c	1011(w)	16	51.1	30.72, 30.72
3C	12 (-RCOO ⁻) ^c	1123(w)	12	76.6	30.72, 34.56
4C	9 (-RCOO ⁻) ^c	1306(w)	9	114.9	34.56, 34.56
1C ^m	24(-RCOO ⁻)/8(-R'CH ₃) ^c	1011(w)	24	34.1	30.72, 30.72
2C ^m	16 (-RCOO ⁻)/16(-R'CH ₃) ^c	1011(w)	16	51.1	30.72, 30.72
3C ^m	12(-RCOO ⁻)/20(-R'CH ₃) ^c	1011(w)	12	68.1	30.72, 30.72
4C ^m	9(-RCOO ⁻)/23(-R'CH ₃) ^c	1011(w)	9	90.8	30.72, 30.72
3C ^{mp}	34(-RCOO ⁻)/14(-RCOOH)/80(-R'CH ₃) ^{c,d}	1917(w)	34	68.1	61.44, 61.44
explicit solvent models (~26% acetonitrile composed aqueous solution)					
3C ^{ms}	12(-RCOO ⁻)/20(-R'CH ₃) ^c	180(a)/500(w)	12	68.1	30.72, 30.72
4C ^{ms}	9(-RCOO ⁻)/23(-R'CH ₃) ^c	180(a)/500(w)	9	90.8	30.72, 30.72
implicit solvent models (aqueous solution approximation, ε = 78.0)					
1C ^{im}	75 (-RCOO ⁻) ^c			38.3	57.60, 57.60
2C ^{im}	64 (-RCOO ⁻) ^c			51.1	61.44, 61.44
3C ^{im}	54 (-RCOO ⁻) ^c			76.6	69.12, 69.12
4C ^{im}	49 (-RCOO ⁻) ^c			114.9	80.64, 80.64
1F ^{im}	75 (-R''COO ⁻) ^c			38.3	57.60, 57.60
2F ^{im}	64 (-R''COO ⁻) ^c			51.1	61.44, 61.44
3F ^{im}	54 (-R''COO ⁻) ^c			76.6	69.12, 69.12
4F ^{im}	49 (-R''COO ⁻) ^c			114.9	80.64, 80.64

^a The number of surface chains, water molecules, acetonitrile molecule and ions(Na⁺), respectively. The 'w' and 'a' represent water molecule and acetonitrile molecule, respectively. ^b In units of Å. The lengths of simulation cells in z direction are used of 300 Å in slab models. ^c R = CH₂CH₂(CH₂)₁₅, R' = (CH₂)₈, R'' = CH₂CH₂(CF₂)₁₅. ^d In 3C^{mp}, we assume only 70% terminated -COOH groups deprotonated in the aqueous solution.

Scheme 4. Surface Models Used in MD Simulations



of the chains' conformations should be considered first. In previous studies of packing structures of alkyl and alkoxy chains modified H-Si(111), it was found that the optimum coverage of long hydrocarbon chains on the H-Si(111) be around of 50%–66.7% due to the van der Waals volumes of hydrocarbon chains and surface atom patterns, which corresponding to around 19.2–25.6 Å² per confined hydrocarbon chain.^{15–19,22,28,29,49–52} So, the smallest space that sufficient for conformational switching of the surface-confined chains is roughly estimated to be around 38 Å² per chain. On the basis of this consideration, nineteen surface models with various solvent backgrounds as listed in Table 1 are constructed in our simulations.

The studied simulation models are illustrated in Scheme 4. The two-dimensional rhombic periodic boundary condition and slab model are applied throughout our simulations.⁵³ Surface models are constructed with the following procedures. First, two kinds of H-Si(111) with surfaces modified by the uniformly distributed amphiphilic chains of the -(CH₂)₁₇COO⁻ (1C–4C) (or the -CH₂CH₂(CF₂)₁₅COO⁻ (1F^{im}–4F^{im})) and by the mixed -(CH₂)₁₇COO⁻ and -(CH₂)₈CH₃ chains (1C^m–4C^m) are constructed by replicating unit cells 'unit 1'–'unit 5', as shown in Scheme 3, in x and y directions. Initially, chains have vertical orientations on surfaces. These constructed surface models are subsequently minimized with surface atoms fixed. After the minimizations,

an upward electric field of $E_{up} = 3.0e9V/m$ is applied to force -COO⁻-terminated surface-confined chains to bend their conformations. When all surface-confined, -COO⁻-terminated chains reaching bent conformations under the applied electric field, the pre-equilibrated, individual solvent layers (containing Na⁺) with the density of 0.998 g/cm³ are put on the top of the bent monolayers. To restrict solvent molecules in the simulation box, a fixed Lennard-Jones (L-J) wall, as shown in Scheme 4, is applied with details given in the next subsection.

2.2. Force Field Models. 2.2.1. Validations of Force Field Calculations. There are many force field models developed to simulate the conformational and aggregative behaviors of the hydrocarbon chains in the bulk phase or confined at the interface, which provide satisfactory descriptions of various properties of hydrocarbon chains.^{54–59} In the present work, we are interested in the conformational behaviors (from the all-trans to the mixture of trans and gauche and its reverse) of the hydrocarbon chains confined at the interface, during which the torsion potential in the force field is considered to be a sensitive factor. The choice of parameters of the torsion term determines the degree of disorder in the hydrocarbon chains and hence directly affects the conformational behaviors of the hydrocarbon chains. A good description of torsional barriers in the alkyl part of chains is thus desirable. To avoid arbitrary results coming from the force field calculations on this kind of switchable surface, we select the cvff,^{54,60} the cff91,^{55,60} and

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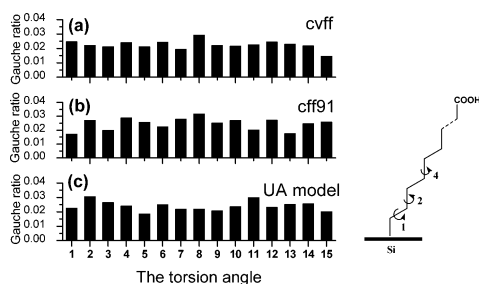


Figure 1. Distributions of gauche defects in the surface-confined chains resulted by the force field models of (a)cvff, (b)cff91, and (c)UA model.

the united atoms (UA)⁵⁶ model with Ryckaert–Bellemans dihedral potential to validate our force field calculations. A surface model contains 48 $-(\text{CH}_2)_{17}\text{COO}^-$ chains is used for this aim, in which the surface-confined chains uniformly distributed with the area per chain of $76.6 \text{ \AA}^2/\text{chain}$ ('unit 3' in Scheme 3). We characterize the equilibrium conformations of surface-confined chains within different force field models with an external electric field of $E_{\text{up}} = 3.0 \times 10^9 \text{ V/m}$ applied. The results are compared in Figure 1, from which we find that the cvff, the cff91, and the UA models predict similar gauche distributions of the surface-confined chains in the bent state. In addition, the average thickness of the monolayer predicted by three force fields are 11.1 \AA (cvff), 11.5 \AA (cff91), and 10.9 \AA (UA model), respectively, which also agree fairly well with each other. Therefore, the cvff and the UA model are used in the following discussions of conformational behaviors of surface-confined chains under external electric fields.

2.2.2. Electric Field Interactions. The external electric field is modeled by

$$V_{\text{ef}} = q_i E_z z_i$$

where q_i is the charge of the i th charged atom, E_z is the electric field strength applied in the z direction, and z_i is the projection of the position vector on the z axis.

2.3 Solvent Models. Two kinds of solvent models, the explicit solvent model and the continuum dielectric model, are used to describe solvent effects.

2.3.1. Explicit Solvent Models. Within the framework of explicit solvent model, two kinds of supporting electrolyte solutions are explicitly considered in our simulations: one consists of water molecules and counterions of Na^+ (**1C-4C**, **1C^m-4C^m**, **3C^{mp}** in Table 1), while another is a mixture of $\sim 26\%$ acetonitrile composed aqueous solution containing Na^+ (**3C^{ms}-4C^{ms}** in Table 1), in which, the water molecules and the acetonitrile molecules are treated by the SPC water model and the cvff that complemented in the *Cerius*² package,⁶⁰ respectively. A L–J 'wall' composed by fixed, single-layered potassium atoms are plainly aligned on the top of the solvent layer to interact with solvent molecules. The cutoff of van der Waals interactions is set to be 12.0 \AA and the electrostatic interaction is evaluated by the Ewald summation.⁶⁰

2.3.2. Continuum Dielectric Models. A continuum dielectric approximation by implicitly considering the solvent molecules and the Na^+ is also introduced ($\epsilon = 78.0$) in our simulations to qualitatively investigate the influences of chains' rigidities on switching behaviors (cf. **1C^{im}-4C^{im}** and **1F^{im}-4F^{im}** in Table 1). The amphiphilic chains of $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-$ (**1C^{im}-4C^{im}**) and $-\text{CH}_2\text{CH}_2(\text{CF}_2)_{16}\text{COO}^-$ (**1F^{im}-4F^{im}**) are treated by the UA model with parameter sets displayed in the Supporting Information.^{56,61,62} In these continuum dielectric models, the long-range Coulombic interactions is cut at a distance of 10 times

of length of the simulation cells in x and y directions, which is thought to be large enough to rationally estimate the Coulombic interactions.

2.4 Molecular Dynamics Simulations. For all calculations, the canonical ensemble (NVT) is applied with systems maintained at 298 K by using of Nosé–Hoover thermostat.⁶³ Equations of the motion for systems are integrated using the velocity Verlet algorithm with the time step of 1 fs .⁵³

2.4.1. Pre-equilibrium. We carry out a series of pre-simulations to generate the 'well' equilibrated distributions of solvent molecules in systems due to the lack of pre-knowledge about them. Starting from the initial conformations as shown in Scheme 4, we first apply the downward electric field $E_{\text{down}} = -2.0 \times 10^9 \text{ V/m}$ on systems in the first 50 ps (0–50 ps) to make surface chains stick their terminal charged carboxylate groups into the solvent layer. A subsequent 50 ps simulation (50–100 ps) without the electric field applied is used to 'relax' the system. After the relaxation period, another 50 ps simulation (100–150 ps) with $E_{\text{up}} = 5.0 \times 10^9 \text{ V/m}$ is carried out to bend the $-\text{COO}^-$ -terminated surface-confined chains. Finally, a 50 ps 'relaxation' simulation (150–200 ps) is performed. To generate reasonable distributions of solvent molecules in the system, these processes are repeated twice.

2.4.2. Production. The simulations in production stages start from the pre-equilibrated surface models, in which the ended $-\text{COO}^-$ groups of surface-confined chains have been fully solvated in the solvent layer with the solvent molecules penetrating into the monolayer to some extents. The switching behaviors of the single-layers modified silicon surfaces are thus conducted by introducing the external electric fields. Much longer simulations are employed to collect MD trajectories. The simulation procedures in these production stages are similar to those used in the **Pre-equilibrium** stages while the simulation time in each electric field upward stage (switching 'off'), surface relaxation stage, and electric field downward (switching 'on') stage are prolonged to 500, 100, and 100 ps, respectively.

3. Results and Discussions

3.1 Switching in the Aqueous Solution. The reversible switching, 'on' and 'off', of the low-density ω -carboxyalkyl monolayers covered H–Si(111), **1C-4C**, and the mixed ω -carboxyalkyl/alkyl monolayers modified H–Si(111), **1C^m-4C^m**, are distinctly observed in the presence of external electric fields within wide ranges of intensities of $-2.0 \times 10^9 \text{ V/m} \leq E_{\text{down}} \leq -0.5 \times 10^9 \text{ V/m}$ and $1.8 \times 10^9 \text{ V/m} \leq E_{\text{up}} \leq 7.3 \times 10^9 \text{ V/m}$, which can be seen directly from snapshots of simulations (Figures 2 and 3) and more quantitatively from the conformational characterizations (Figure 4) such as the gauche ratio, the thickness of monolayer ($t_{\text{monolayer}}$), etc.

3.1.1. Switching 'on'. In periods that directions of applied electric fields are downward, surfaces **1C-4C** and **1C^m-4C^m** are turned 'on'. The terminated carboxylate groups are forced to move upward for their negative charges, which make $-\text{COO}^-$ -terminated surface-confined chains stretch straightly and consequently take a nearly all-trans equilibrium conformation as in **1C_(on)-4C_(on)** and **1C^m_(on)-4C^m_(on)** with terminal charged carboxylate groups standing on the top of monolayers (cf. Figures 2 and 3). It can be found that in a broad range of intensities of applied fields, $-2.0 \times 10^9 \text{ V/m} \leq E_{\text{down}} \leq -0.5 \times 10^9 \text{ V/m}$, the $-\text{COO}^-$ -terminated surface-confined chains demonstrate conformational transitions from the bent state (switching 'off') to straight conformations (switching 'on') as depicted in Figure 4. Actually, the bent surface-confined chains almost spontaneously relax conformations to the straight ones

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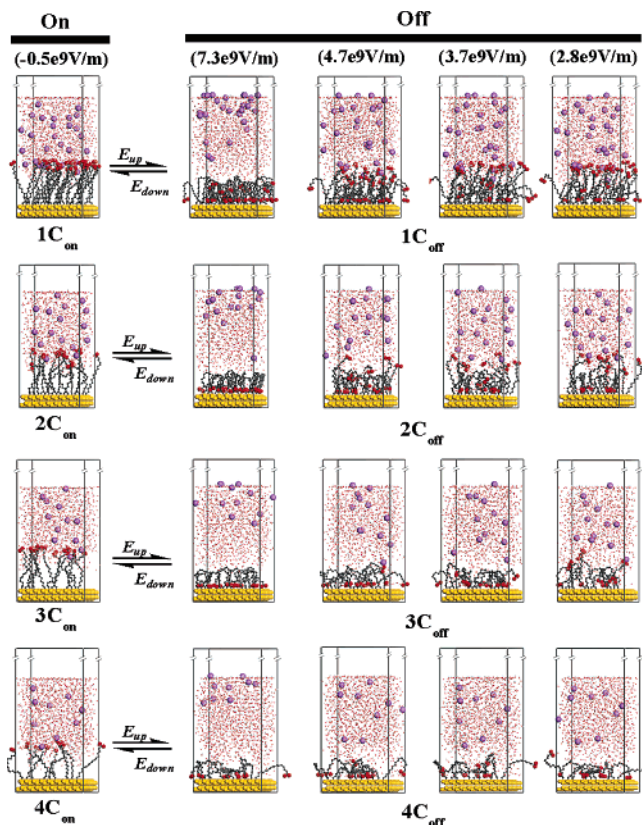


Figure 2. Simulation snapshots of the single-layer, $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-$ modified H-Si(111), **1C-4C**. The red and purple CPK models represent the $-\text{COO}^-$ groups and the Na^+ , respectively. The H atoms in the surface chains are removed for the clarity.

even without the external electric field applied, due to the preference of all-trans conformations in hydrocarbon chains. The dominant trans conformations in switching ‘on’ states are also reflected by small gauche ratios of no more than 0.15 and thickness of monolayers, $t_{\text{monolayer}}$, of about ~ 20 Å for **1C-4C** and **1C^m-4C^m** from Figure 4. Thus, in these switching ‘on’ periods, surfaces **1C-4C** and **1C^m-4C^m** are thought to be in the hydrophilic state because the hydrophilic groups of carboxylate anions are the outermost groups of monolayers, which directly interact with surrounding aqueous solutions.

3.1.2. Switching ‘off’. In contrast to spontaneous transitions of surface chains from the bent ‘off’ state to the straight ‘on’ conformations, the reverse process, ‘on’ \rightarrow ‘off’, is thought to be much more difficult as it is necessary to overcome high energy barriers mainly contributed by the energy penalty for trans-gauche conformational transitions, the steric hindrances aroused by surrounding solvent molecules and neighboring hydrocarbon chains, as well as some intrinsic hindrances in this kind of switching surface. To probe the value of the *critical intensity* that enables the realization of switching ‘off’ states in **1C-4C** and **1C^m-4C^m**, several intensities of electric fields, $E_{\text{up}} = 7.3 \times 10^9$, 4.7×10^9 , 3.7×10^9 , 2.8×10^9 , and 1.8×10^9 V/m, are investigated in our simulations.

A dependence of switching behaviors of surfaces **1C-4C** and **1C^m-4C^m** on intensities of applied electric fields is distinctly observed in Figures 2–4. At the high intensity of $E_{\text{up}} = 7.3 \times 10^9$ V/m, all surface models **1C-4C** and **1C^m-4C^m** exhibit significant transitions of surface-confined chains. The electric field at this intensity is strong enough to drag all carboxylate

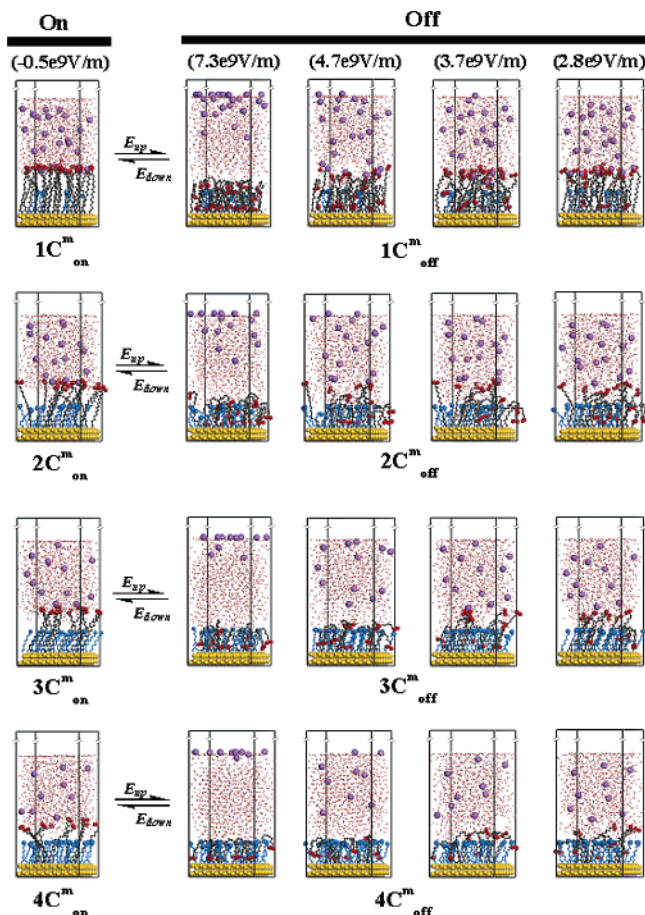


Figure 3. Simulation snapshots of the mixed $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-/-\text{CH}_2(\text{CH}_2)_7\text{CH}_3$ modified H-Si(111), **1C^m-4C^m**. The red and purple CPK models represent the $-\text{COO}^-$ groups and the Na^+ , respectively. The blue chains in figures represent short alkyl chains of $-\text{CH}_2(\text{CH}_2)_7\text{CH}_3$. The H atoms in the surface chains are removed for the clarity.

groups from the monolayer/water interfaces to the deeper parts of the monolayers for all surfaces **1C-4C** and **1C^m-4C^m** with various densities of surface-confined chains. However, the electric field at this strength may be too strong to be realistic in the practical applications. Decreasing the intensity of the electric field to the moderate one, i.e., $E_{\text{up}} = 4.7 \times 10^9$ V/m, we find the number of conformational changed chains significantly decrease for surfaces **1C-2C** and **1C^m-2C^m** with higher coverage of $-\text{COO}^-$ -terminated chains, in which, some carboxylate groups still keep their positions around monolayer/water interfaces when systems reaching the equilibrium ‘off’ states (cf. Figures 2 and 3). The similar tendency is also found for those lower densities $-\text{COO}^-$ -terminated chains modified H-Si(111) of **3C-4C** and **3C^m-4C^m** when intensities of electric fields are lowered to $E_{\text{up}} = 3.7 \times 10^9$ V/m and $E_{\text{up}} = 2.8 \times 10^9$ V/m as shown in Figures 2 and 3. As a result, hydrophobic properties of surfaces **1C-4C** and **1C^m-4C^m** in the switching ‘off’ states are weakened for the accumulation of increasingly more hydrophilic $-\text{COO}^-$ groups around monolayer/water interfaces accompanied by the decrease in the strength of E_{up} . Even though, all surfaces **1C-4C** and **1C^m-4C^m** are still considered to have wettabilities changed in these ‘off’ states, since the terminal hydrophilic $-\text{COO}^-$ groups are forced to immerse into the hydrophobic monolayers more or less and the hydrophobic parts of surface chains are exposed to water layers directly.

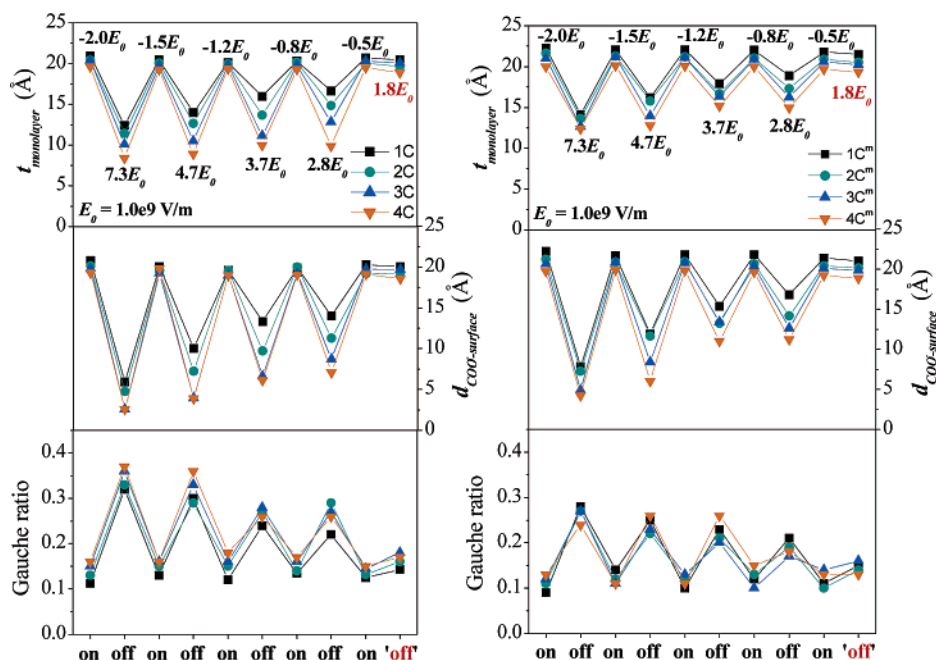


Figure 4. Characterizations of switching behaviors, ‘on’ and ‘off’, of (a) evenly distributed, single-layer $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-$ modified silicon surfaces (**1C–4C**) and (b) mixed $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-/-\text{CH}_2(\text{CH}_2)_7\text{CH}_3$ modified silicon surfaces (**1C^m–4C^m**). The units are in Å for average distances between the terminal $-\text{COO}^-$ groups and the silicon surface ($d_{\text{COO}^- \text{-surface}}$) and average thicknesses of monolayers ($t_{\text{monolayer}}$). The gauche defect is defined as the torsion angle differs by more than $\pm 60^\circ$ from that of the all-trans conformation ($\pm 180^\circ$). The lines are drawn as a guide to the eye.

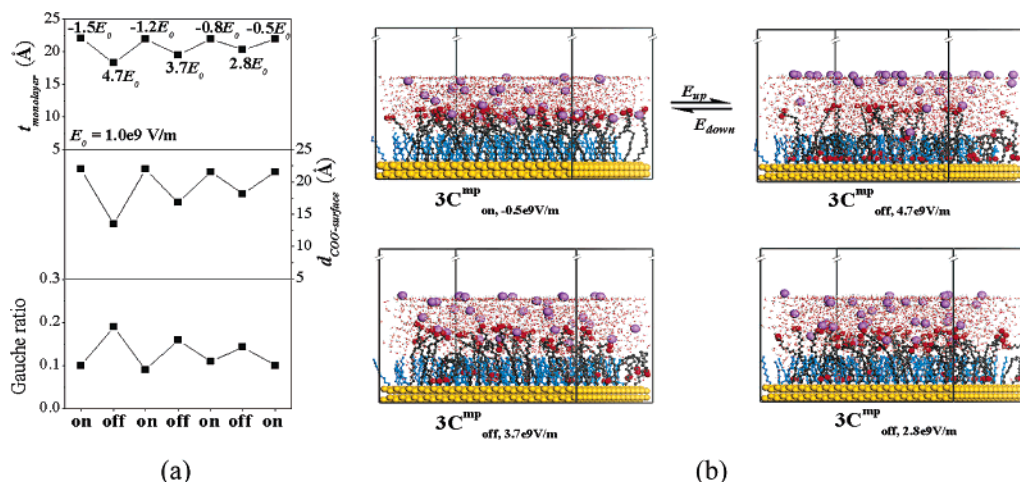


Figure 5. (a) Characterizations and (b) simulation snapshots of the partially (70% dissociations of the $-\text{COOH}$ groups) dissociated, mixed $-\text{CH}_2(\text{CH}_2)_{16}\text{COOH}/-\text{CH}_2(\text{CH}_2)_7\text{CH}_3$ modified H-Si(111), **3C^{mp}** (cf. Table 1). The red and purple CPK models represent the $-\text{COO}^-$ groups and the Na^+ , respectively. The blue chains in figures represent short alkyl chains of $-\text{CH}_2(\text{CH}_2)_7\text{CH}_3$. The H atoms in the surface chains are removed for the clarity.

Further decreasing the E_{up} to 1.8×10^9 V/m, conformational changes of surface chains are not observed for all surfaces **1C–4C** and **1C^m–4C^m** (cf. Figure 4). The $E_{\text{up}} = 1.8 \times 10^9$ V/m is theoretically predicted as the *critical intensity* that needed to trigger the switch. The *critical intensity* of the electric field can be further rationalized by some factors, which will be discussed in the next section.

3.1.3. Influence of Surface pK_a Value. As mentioned above, we have neglected partial dissociations of surface carboxylic acids in surface models **1C–4C** and **1C^m–4C^m**. In real situations, the $-\text{COOH}$ -terminated monolayers often undergo the incomplete deprotonations in the electrolyte solution.^{39,40,43,46,47,64,65} The pK_a of the acid-bearing monolayers depends strongly on the pH value of the solution and the interfacial dielectric environments. In the latest studies of acid-bearing silicon surfaces, the surface pK_a is estimated to be around $\sim 9 \pm 1$ at

the pH value of 11.2 of the aqueous solution, corresponding to $\sim 75\%$ surface $-\text{COOH}$ groups dissociated into $-\text{COO}^-$ in the electrolyte solutions.^{39,47} On the basis of this consideration, we further observe switching behaviors of the partially dissociated, carboxylic acid-terminated monolayers modified surface model of **3C^{mp}** (cf. Table 1), in which, we assume only 70% surface $-\text{COOH}$ groups are ionized into the $-\text{COO}^-$. From Figure 5, by employing external electric fields, switching of surface **3C^{mp}** is also distinctly observed, similar to those fully dissociated, carboxylic acid modified surfaces **1C–4C** and **1C^m–4C^m**. This indicates the undissociated $-\text{COOH}$ -terminated chains exert small influences on conformational switching of monolayers. Surface in such a partially dissociated situation is also expected to change surface wettability between the hydrophilic state and the moderately hydrophobic state in response to the electric fields with properties intensities.

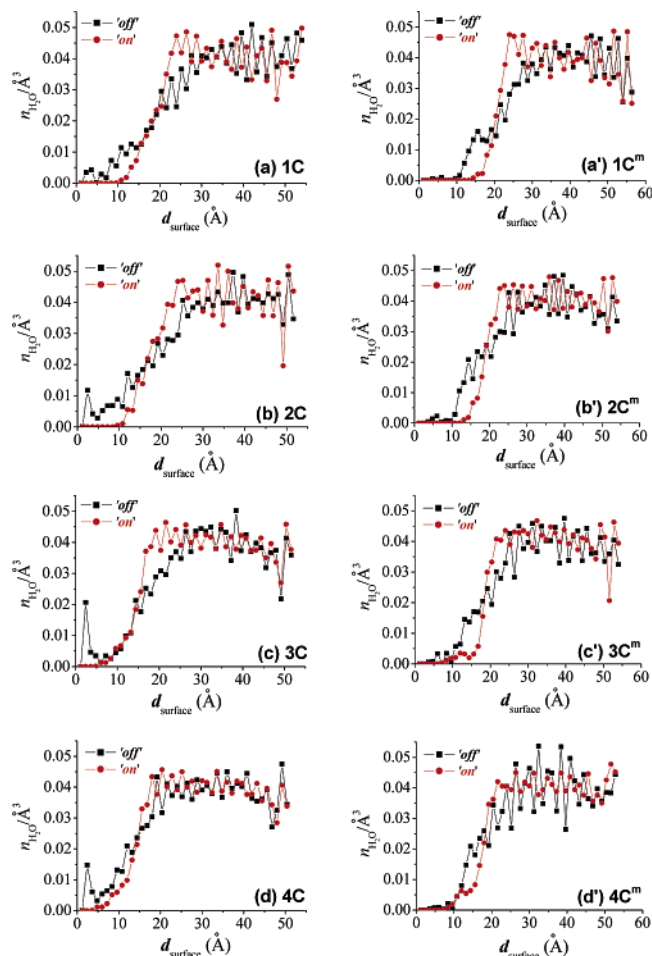


Figure 6. Plots of the average number density of water molecules ($n_{\text{H}_2\text{O}}/\text{\AA}^3$) as the function of the vertical distance relative to the silicon surface (d_{surface}). The statistic of number of water molecules is at interval of 1.2 \AA . Curves (a)–(d) and (a')–(d') represent distributions of water molecules in surface models **1C–4C** and **1C^m–4C^m**, respectively. $E_{\text{up}} = -0.5 \times 10^9$ V/m, $E_{\text{down}} = 4.7 \times 10^9$ V/m.

3.1.4. Changes in Distributions of Water Molecules. The reorganizations of solvent molecules at monolayers/water interfaces are observed in switching processes from Figure 6, which are caused by conformational changes of chains and effects of external electric fields. Our simulation results indicate water molecules penetrated into the hydrophilic part of monolayers to different extents for surfaces **1C–4C** and **1C^m–4C^m** in both switching ‘on’ and ‘off’ states. A rapid decrease in densities of water molecules is found when d_{surface} is less than ~ 20 \AA , which is approximated to be the height of switching ‘on’ monolayers, for all surface models **1C–4C** and **1C^m–4C^m**. Going far from silicon surfaces ($d_{\text{surface}} > 20$ \AA), distributions of water molecules are similar to those natural water distributions in initial sets, reflecting the hydrophobic essence of inner hydrocarbon monolayers.

During switching ‘off’ stages, from Figure 6, water molecules move down in accompany with the bending of monolayers. We notice a little amount of water molecules are ‘captured’ in the deeper part of bended hydrophobic monolayers for those evenly distributed $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-$ modified H–Si(111) of **1C–4C** as shown in Figure 6. The effects of interactions between the silicon surfaces and the water molecules in surface models **1C–4C** will be discussed later in Section 4.

3.2 Factors Affecting Switching. Up to now, we have depicted a picture of switching ‘on’ and ‘off’ behaviors of low-density, $-\text{COOH}$ -terminated monolayers modified H–Si(111) in the aqueous solution by gradually tuning intensities of external electric fields. Both series of H–Si(111) with uniformly distributed $-(\text{CH}_2)_{17}\text{COO}^-$ chains (**1C–4C**) and mixed $-(\text{CH}_2)_{17}\text{COO}^-/-(\text{CH}_2)_8\text{CH}_3$ substitutions (**1C^m–4C^m**) exhibit distinctly switching behaviors under broad ranges of applied electric fields, -2.0×10^9 V/m $\leq E_{\text{down}} \leq 0$ and $E_{\text{up}} > 1.8 \times 10^9$ V/m.

However, differences in switching behaviors of surfaces with different densities of $-\text{COO}^-$ -terminated surface-confined chains are distinctly observed. From Figure 4, switching capabilities of surfaces **1C–2C** and **1C^m–2C^m** decay rapidly with the decrease in the strength of the electric field in the ‘off’ stages in comparison to those $-\text{COO}^-$ -terminated chains modified H–Si(111) of **3C–4C** and **3C^m–4C^m** in lower density. To gain insights into the relationship between the switching performance and surface patterns, some important factors such as the steric hindrances, the formation of the interfacial electric double layer, the hydration effect of carboxylate anions, as well as influences of components of the surrounding electrolyte solutions and the rigidity of surface-confined chains are discussed as follows.

3.2.1 Steric Hindrances. As addressed before, a basic criterion in the design of switching surfaces is to provide sufficient freedoms for conformational transitions of surface-confined chains.³ During a switching process, steric hindrances aroused from the neighboring surface-confined chains and solvent molecules exert great influences on the conformational behaviors of chains. At the occurrence of conformational transitions, the limited inter-carboxyalkyl chains’ spaces in surfaces **1C–2C** (38.3 $\text{\AA}^2/\text{chain}$ – 51.1 $\text{\AA}^2/\text{chain}$) and **1C^m–2C^m** (34.1 $\text{\AA}^2/\text{chain}$ – 51.1 $\text{\AA}^2/\text{chain}$) maximize the interchain’s interactions and also restrict motions of chains. The bended ‘osier’ structures are formed for those conformational changed chains, which occupy larger spaces in the deeper part of monolayers and hence make the further bending of chains more difficult. In contrast, loosely distributed chains in **3C–4C** (76.6 $\text{\AA}^2/\text{chain}$ – 114.9 $\text{\AA}^2/\text{chain}$) and **3C^m–4C^m** (68.1 $\text{\AA}^2/\text{chain}$ – 90.8 $\text{\AA}^2/\text{chain}$) provide much more amplitude spaces for steric relaxations of bent chains in switching ‘off’ stages, achieving thinner monolayers of around 9 – 10 \AA relative to those **3C–4C** and **3C^m–4C^m** (11 – 12 \AA) and broader distributions of the gauche defects in chains (Figure 4 and Figure S1 and S2). Therefore, the flexible space of at least ~ 40 \AA^2 and more preferable in the range of 70 – 90 \AA^2 per carboxyalkyl chain that available for the conformational change of the surface-confined chains should be first considered in the design of the carboxyalkyl or mixed alkyl/carboxyalkyl monolayers modified switching surfaces. In fact, the reported Au based switching surfaces were realized with the area of ~ 65 \AA^2 per carboxyalkyl chain.³

3.2.2 Electrostatic Interactions. Two main effects that aroused by the electrostatic interactions between the negatively charged $-\text{COO}^-$ groups and the surrounding polar species (such as the water molecules and the Na^+ ions) are responsible for the observed dependence of conformational switching on the strength of the external electric field. One is the interfacial potential at the monolayer/aqueous solution interface and another is the ionic solvation energetics in the interfacial microenvironment. Both effects have been invoked to explain the acid/base properties of acid-bearing monolayers at interfaces.^{64,65}

3.2.2.1. Interfacial Electrical Double Layers. Interfacial electrostatic potentials originating from ionizations of carboxylic acid groups at the monolayers/aqueous solution interface were detected and discussed by many groups.^{40,47,65–68} By using surface electrostatic models, Lochhead et al. illustrated a picture of ion distributions at the charged monolayer/electrolyte solution interface, which demonstrated that the interfacial electrical double layer was formed in the presence of interfacial electrostatic potentials.⁶⁸ In our simulations of surfaces **1C-4C** and **1C^m-4C^m**, from Figures 2 and 3, interfacial electrostatic potentials are also found according to equilibrium distributions of negatively charged carboxylate groups at the monolayer/aqueous solution interfaces in switching ‘on’ stages (**1C_{on}-4C_{on}** and **1C^m_{on}-4C^m_{on}**). Obviously, such interfacial potentials depend straightly on densities of interfacial-confined carboxylate groups, which strongly interact with the neighboring Na⁺ in solvent layers and consequently induce formations of electrical double layers at monolayers/water interfaces. Upon formations of these interfacial electrical double layers, some Na⁺ are strongly electrostatically attracted by carboxylate anions in the ‘Stern layer’ as shown in Scheme 2,⁶⁸ restricting the mobility of those bound carboxylate groups. Simultaneously, the electrostatic attractions derived from the distribution of Na⁺ in the ‘diffusing layer’ also counteract partial electrostatic interactions of the external electric fields.

As expected, influences of interfacial electrical double layers are much more significant for surfaces with higher concentrations of interfacial-confined carboxylate groups (**1C-2C** and **1C^m-2C^m**). As seen from Figures 2 and 3, many carboxylate anions in surfaces **1C-2C** and **1C^m-2C^m** are electrostatic bound by Na⁺, forming the –COO[–]Na⁺ ionic pairs in the Stern layer. Under electric fields with moderate intensities, such as $E_{\text{up}} = 3.7 \times 10^9$ and 2.8×10^9 V/m, driving forces resulted from electric fields are obviously too weak to overcome electrostatic attractions between the –COO[–] group and the Na⁺ and hence conformational changes of –COO[–]-terminated surface-confined chains on surfaces **1C-2C** and **1C^m-2C^m** happen reluctantly. On the contrary, for surfaces **3C-4C** and **3C^m-4C^m** with lower densities of –COO[–]-terminated chains, moderate intensities of electric fields, 2.8×10^9 V/m $\leq E_{\text{up}} \leq 3.7 \times 10^9$ V/m are shown to be strong enough to cause *global* conformational transitions of –COO[–]-terminated chains. In fact, the –COO[–]Na⁺ ionic pairs may be dissociated or reformed along with evolutions of systems under external electric fields: they are fully destroyed when the strength of the electric field is increased to $E_{\text{up}} = 7.3 \times 10^9$ V/m (unrealistic) for all surfaces **1C-4C** and **1C^m-4C^m**.

Thus, the much more difficult occurrence of switching of surfaces **1C-2C** and **1C^m-2C^m** in higher densities of surface chains may be caused by not only larger steric hindrances (as addressed in Subsection 3.2.1) but also stronger electrostatic interactions than those of **3C-4C** and **3C^m-4C^m**.

3.2.2.2. Carboxylate Anion Hydration. The hydration of the carboxylate anion is an essential factor affecting the acidic dissociation equilibrium.^{40,46(b),65} As assumed in Scheme 2, to make a surface switches from the hydrophilic ‘on’ state to the

hydrophobic ‘off’ state, a key step is to force the carboxylate groups to transfer their positions from the higher dielectric medium of the monolayer/aqueous solution interface to the inner hydrocarbon part of the monolayer with low dielectric constant. In such a process, it has to overcome an energy penalty to move the carboxylate groups, which is noted as ‘desolvation energy’.⁶⁹ From the solvation point of view, the transfer of carboxylate anions from the hydration state to the inner part of a monolayer is an energy uphill process due to the need to shed ions’ solvation shell and displace the water molecules with the hydrophobic methylene groups.

A thermodynamics model that proposed by Aydogan et al. is introduced to estimate the energy changes in the switching process.⁷⁰ Here, we manage to derive the desired intensity of the external stimulus for driving the switch on the basis of our MD simulation results and to further elucidate contributions of various factors. In a first-order approximation, we neglect the interaction of the silicon surface and assume the negatively charged carboxylate groups act as dynamically mobile acceptors in response to external stimuli such as the electric field, which will cause reorientations of –COO[–]-terminated chains. The change in Gibbs free energy $\Delta G_{\text{total}}(\text{‘on’} \rightarrow \text{‘off’})$ upon transitions of a system from the switching ‘on’ state to the switching ‘off’ state in the aqueous medium is represented as follows⁷⁰

$$\Delta G_{\text{total}}(\text{‘on’} \rightarrow \text{‘off’}) = \Delta G_{\text{conf}}(\text{‘on’} \rightarrow \text{‘off’}) + \Delta G_{\text{sur}}(\text{‘on’} \rightarrow \text{‘off’}) + \Delta G_{\text{hyd}}(\text{‘on’} \rightarrow \text{‘off’}) + \Delta G_{\text{ele}}(\text{‘on’} \rightarrow \text{‘off’}) \quad (1)$$

where $\Delta G_{\text{conf}}(\text{‘on’} \rightarrow \text{‘off’})$ is the change of Gibbs free energy associated with internal conformational reorientations of the chains (from all-*trans* to mixed *trans/gauche*) and can be approximated as $0.9 nkT$ with n being the number of gauche-reorientation bonds in the switching ‘off’ state and k is the Boltzmann constant.⁷⁰ $\Delta G_{\text{sur}}(\text{‘on’} \rightarrow \text{‘off’})$ reflects interactions of hydrocarbon chains in monolayers and their interactions with the surrounding solvent molecules, which is approximately taken as $1.5mkT$, where m is the number of methylene groups that exposure to the surrounding aqueous solution when the electric field is applied.⁷⁰ $\Delta G_{\text{hyd}}(\text{‘on’} \rightarrow \text{‘off’})$ represents energy penalty for the transition of the carboxylate anion from the higher dielectric medium (aqueous phase, $\epsilon = 78.0$) to the lower dielectric medium of the monolayers surface ($\epsilon \sim 14.0$),⁶⁵ which is estimated to be $10.2kT$ (25.3 kJ/mol) from the Born model.^{71–73} $\Delta G_{\text{ele}}(\text{‘on’} \rightarrow \text{‘off’})$ is composed of electrostatic contributions from external electric fields and the work performed to transfer the isolated charges (Na⁺) dispersed in the bulk solution to the charged monolayer surface, which can be approximately described by $e\psi_0 + e\psi_m$,⁷⁰ where e is the electronic charge, ψ_0 and ψ_m is the electrode potential and the membrane potential, respectively. According to our MD simulations, two gauche-reorientation bonds are observed on average ($n = 2$, $m = 2$) in each conformational changed chain. Approximately, $\psi_m = -53.0$ mV is taken according to previous studies of carboxylic acid-terminated self-assemble monolayers.⁶⁷ So, the $\Delta G_{\text{total}}(\text{‘on’} \rightarrow \text{‘off’})$ defined in eq 1 is evaluated as

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$$\Delta G_{\text{total}(\text{on}'\rightarrow\text{off}')} \approx 1.8kT + 3.0kT + 10.2kT + 2.1kT - e\psi_0 \quad (2)$$

To trigger the switching process, 'on' \rightarrow 'off' ($\Delta G_{\text{total}(\text{on}'\rightarrow\text{off}')} \leq 0$), the required surface potential is estimated to be $\psi_0 \geq 0.44$ V at 298 K, which may be achievable in experimental conditions and well correlated with previous studies of Au based switching surfaces.³

3.2.3 Interfacial Dielectric Medium. The effects discussed above are based on two distinct physical phenomena, which are not entirely independent, since the distribution of interfacial potentials depends in part on the dielectric medium at the interface. In fact, these effects have been invoked by many authors to apprehend the unique acid/base equilibrium of carboxylic acid-bearing monolayers in the aqueous solution.^{40,46(b),65} For example, it was found that interfacial micro-environments surrounding carboxylic acid groups strongly affected the solvation energetics of carboxylate anions.⁶⁵ These observations remind us a possible way to control the surface switching by adjusting the interfacial dielectric medium.

As assessed in eq 2, the hydration effect of the carboxylate anion is a dominant contribution of the energy change in a switching process. The alternation of the component of the coating solution is thus considered to be a possible way to decrease the energy penalty of the $\Delta G_{\text{hyd}(\text{on}'\rightarrow\text{off}')}$ (eq 1), hence lowering the value of the *critical intensity* of the electric field in the switching process.

The increase of the ionic strength in the surrounding electrolyte solution may be unfavorable, since much more positive ions will be bound to carboxylate anions at the interface and consequently weaken switching capabilities of surfaces. A low ionic strength in the coating solution is thus desirable to facilitate the switching.

In present work, the water-soluble acetonitrile molecules are introduced in models **3C^{ms}** and **4C^{ms}** (cf. Table 1), in which a ~26% acetonitrile molecules composed aqueous solution is employed. The addition of acetonitrile molecules into the aqueous solution is expected to destroy strong hydrogen-bond network between water molecules and $-\text{COO}^-$ anions and hence lower hydration effects of carboxylate groups at monolayers/electrolyte solution interfaces. Switching behaviors of surfaces **3C^{ms}-4C^{ms}** at $E_{\text{up}} = 1.8 \times 10^9$ V/m (the *critical intensity* in the aqueous solution), can be still distinctly observed as shown in Figure 7, indicating the hydration effect of carboxylate groups is effectively lowered by the accumulation of the acetonitrile molecules at the monolayers/electrolyte interface. The alternation of molecular components of the electrolyte solution may be an efficient way to adjust the *critical intensity* of the electric field for switches.

3.2.4 Rigidity of Surface-Confining Chains. From previous experimental and theoretical experiences, the introduction of the fluorinated parts of $-\text{CF}_2-$ groups into the hydrocarbon amphiphilic chains can increase the stiffness of the amphiphilic chains and greatly affect packing structures and electric properties of monolayers they formed.^{61,74}

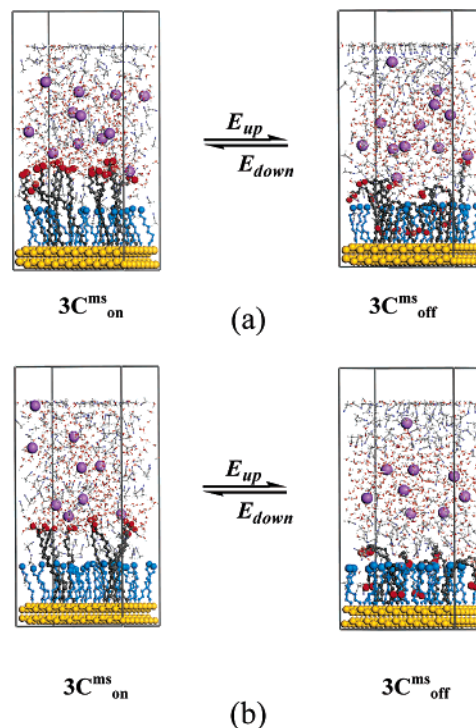


Figure 7. Simulation snapshots of switching behaviors, 'on' and 'off', of mixed $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-/-\text{CH}_2(\text{CH}_2)_7\text{CH}_3$ modified H-Si(111), **3C^{ms}-4C^{ms}**, in the ~26% acetonitrile composed aqueous solution under external electric fields of $E_{\text{up}} = 1.8 \times 10^9$ V/m and $E_{\text{down}} = -0.5 \times 10^9$ V/m. The red and purple CPK models represent $-\text{COO}^-$ groups and Na^+ , respectively. The blue chains in figures represent short alkyl chains of $-\text{CH}_2(\text{CH}_2)_7-\text{CH}_3$.

In present, two series of surface models, **1C^{im}-4C^{im}** and **1F^{im}-4F^{im}** (cf. Table 1), within the frameworks of the UA model and the continuum dielectric approximation are investigated to qualitatively examine the influence of chains' rigidity on conformational behaviors of surface-confined chains. The conformational properties as well as snapshots of surfaces under electric fields are displayed in Figure 8 and Figures S3 and S4 in the Supporting Information, respectively. In comparison with those alkyl monolayers modified H-Si(111) (**1C^{im}-4C^{im}**), conformational transformations of fluorinated chains (**1F^{im}-4F^{im}**) in response to the electric field are much more difficult due to the higher trans-gauche torsional barriers of $-\text{CF}_2-\text{CF}_2-$ fragments. Moreover, fluorinated monolayers demonstrate much more order characters, which can be seen from Figure 8 that the gauche ratios (0.15–0.20) of fluorinated monolayers are greatly smaller than those (0.26–0.32) of alkyl composed monolayers when surfaces are restricted in the 'off' states. This agrees well with our chemical intuitions.

On the other hand, the facile transitions of conformations of surface chains in **1C^{im}-4C^{im}** and **1F^{im}-4F^{im}** under moderate intensities of electric fields, $E_{\text{up}} = 2.8 \times 10^9$ and 3.7×10^9 V/m, may be ascribed to the neglects of the steric hindrance of

(71) The change of free energy in transferring of a carboxylate anion from the aqueous solution (phase 1) to the monolayer/water interface (phase 2) can be simply estimated from the Born model (ref 72) that $\Delta G_{\text{trans},1-2} = q^2/8\pi\epsilon_0 r (1/\epsilon_2 - 1/\epsilon_1)$, where q is ion's charge and ϵ_0 is the vacuum dielectric constant. Substituting value of 1.61 Å for the radius r of acetate (ref 73) and 78.0, 14.0 (ref 65) for the relative constant ϵ_1 and ϵ_2 , respectively, we obtain $\Delta G_{\text{trans},1-2} = 10.2$ kJ/mol.

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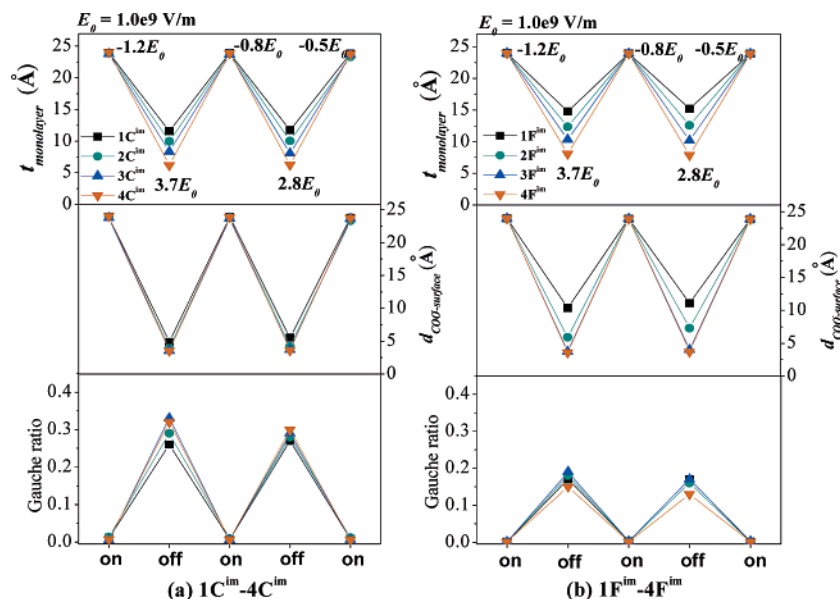


Figure 8. Characterizations of switching behaviors, ‘on’ and ‘off’, of (a) $-\text{CH}_2(\text{CH}_2)_{16}\text{COO}^-$ ($1\text{C}^{\text{im}}\text{-}4\text{C}^{\text{im}}$) and (b) $-\text{CH}_2\text{CH}_2(\text{CF}_2)_{15}\text{COO}^-$ ($1\text{F}^{\text{im}}\text{-}4\text{F}^{\text{im}}$) substituted silicon surfaces in the continuum dielectric approximations. The units are in Å for the average distances between the terminal $-\text{COO}^-$ groups and the silicon surface ($d_{\text{COO}^- \text{-surface}}$) and the average thickness of monolayers ($t_{\text{monolayer}}$). The gauche defect is defined as the torsion angle differs by more than $\pm 60^\circ$ from that of the all-trans conformation ($\pm 180^\circ$). The lines are drawn as a guide to the eye.

solvent molecules and the interactions of positive cations within the continuum dielectric approximation.

4. Surface Patterns in Practical Considerations

Although the reversibly switching behaviors of these low density $-\text{COO}^-$ -terminated H-Si(111) in response to external electric fields are demonstrated by our simulations, there are still some considerations should be addressed when we try to apply these surface designs into practice. Up to now, the experimental way to achieve electric fields in the aqueous solution is to perform electrochemical experiments, in which, the electrical double monolayers is expected to form on the electrode surface. Simultaneously, the oxidization/reduction of water molecules and erosions of silicon surface by water molecules may occur when water molecules directly contact with the silicon surface.

On the basis of these considerations, the surface pattern that H-Si(111) modified by the mixed ω -carboxyalkyl/alkyl monolayers (such as $1\text{C}^{\text{m}}\text{-}4\text{C}^{\text{m}}$) is considered to be a more plausible design of silicon surface based switches. The first reason is that the surface pattern of mixed ω -carboxyalkyl/alkyl modified H-terminated silicon surfaces has been experimentally characterized.⁴⁰ Moreover, the short alkyl chains in the mixed ω -carboxyalkyl/alkyl monolayers may exert great protections on the silicon surface in electrochemical environments, which effectively prevent contacts between water molecules and the electrode and thus stabilizing the system in electrochemical environments. Taking the steric hindrances and the electrostatic interactions into further considerations, the optimum mole fraction of $N_{-(\text{CH}_2)_{17}\text{COOH}} : N_{-(\text{CH}_2)_8\text{CH}_3} = 0.4\sim 0.6$ (corresponding to $70\sim 90 \text{ \AA}^2$ per carboxyalkyl chain) is suggested to facilitate conformational switching of surface chains.

Conclusions

We theoretically demonstrate switching behaviors of a series of carboxylic acid-terminated monolayers modified H-Si(111) in the presence of external electric fields. It has been found in

wide ranges of intensities of electric fields, $-2.0 \times 10^9 \text{ V/m} \leq E_{\text{down}} \leq 0$ and $E_{\text{up}} \geq 1.8 \times 10^9 \text{ V/m}$, both series of surface models containing uniformly distributed, $-(\text{CH}_2)_{17}\text{COOH}$ modified H-Si(111) ($1\text{C}\text{-}4\text{C}$, etc.) and the mixed $-(\text{CH}_2)_8\text{CH}_3/-(\text{CH}_2)_{17}\text{COOH}$ modified H-Si(111) ($1\text{C}^{\text{m}}\text{-}4\text{C}^{\text{m}}$, etc) exhibit distinct conformational switching. Correspondingly, surfaces reversibly switch wettabilities from the hydrophilic switching ‘on’ state to the moderately hydrophobic switching ‘off’ state.

The intensity of the applied electric field and coverage of carboxyalkyl chains significantly affect performances of switches. A *critical intensity* of $E_{\text{up}} = 1.8 \times 10^9 \text{ V/m}$ is observed in our simulations to trigger switches in the aqueous solution. The existence of the *critical intensity* of the electric field in the switching process is rationalized by a basic thermodynamical model, from which, the hydration effect of the carboxylate anion ($-\text{COO}^-$) is assessed to be an important contribution of the change of the free energy in a switching process. Other effects that underlying this kind of carboxylic acid-monolayers modified switching surface, such as the steric hindrances and the electric double layers formed at the monolayers/water interface, are also elucidated to account for the dependence of switching capabilities of surfaces on strengths of electric fields. Simultaneously, our simulations indicate that it is possible to lower the value of *critical intensity* of the electric field (or electric potential) in switching processes via altering components of coating electrolyte solutions. The lower ionic strength and additions of acetonitrile molecules in the surrounding aqueous solution may facilitate the switching under external electric fields. In addition, the introduction of fluorinated parts of more stiffness $-\text{CF}_2-\text{CF}_2-$ fragments into surface chains makes the bend of surface molecules much more difficult.

To summarize, these simulations allow us to suggest an optimum design of the switching surface. In general, to obtain the desired switching performance of the charged groups-terminated monolayers modified surface, two most important factors, the coverage of surface-confined molecules and the

component of the coating electrolyte solution should be considered. A proper coverage of surface-confined molecules may lower hindrances of steric effects and electrostatic interactions in the switching process. Our simulation results indicate that the area per surface-confined molecule $>40 \text{ \AA}^2$ is a basic criterion that permits the constructions of switches. At present, an optimum surface pattern that H-Si(111) modified by the mixed ω -carboxyalkyl/alkyl monolayers (such as **1C^m-4C^m**) in mole fraction of $N_{-(\text{CH}_2)_{17}\text{COOH}} : N_{-(\text{CH}_2)_8\text{CH}_3}$ of around 0.4~0.6 (corresponding to 70~90 \AA^2 per carboxyalkyl chain) is theoretically suggested. On the other hand, the coating solution that has low solvation effects for ions and in lower ionic strength may facilitate the switching. For example, a ~26% acetonitrile composed aqueous solution has been demonstrated to be able to trigger switches even the intensity of the electric field is lower than the observed *critical intensity* of $E_{\text{up}} = 1.8 \times 10^9 \text{ V/m}$. In

addition, the development of a polarizable force field to describe the polarization of molecules in response to the external electric field is of urgent importance, which deserves our efforts toward this direction.

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Supporting Information Available: The parameter sets for the UA model and simulation results of continuum dielectric models **1C^{im}-4C^{im}** and **1F^{im}-4F^{im}** are available in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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