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Macroscopic superhydrophobicity achieved by atomic decoration with silicones

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Modulating wetting states of water droplets on a solid surface has great potential in numerous applications such as self-cleaning, heat transfer, and water purification. Present strategies to achieve controlled wettability usually employ surface roughness and/or chemical coating at the nanometer-to-micrometer scale. Here we propose that atomic-scale decoration and patterning with silicones can be used to fabricate superhydrophobic surfaces. Atomic decoration, differing from chemical coatings in the characteristic size and partial coverage, controls wetting states with the atomic precision (several angstroms) at low cost and maintains a long lifetime. We attribute the mechanism of atomic decoration to the decrease in *effective potential-well depth*, inducing weak interactions between the substrate and water droplet. Our work pushes water wetting to the limit of atomic scales, hinting for a paradigm shift from macroscopic to atomically-precise engineering of wetting states and providing new insights for fabricating superhydrophobic surfaces. *Published by AIP Publishing.* https://doi.org/10.1063/1.5030758

INTRODUCTION

Wetting states of water droplets on solid surfaces are ubiquitous in nature (for example, dew sliding off leaves) and play critical roles in industries. Among a variety of exotic wetting states, superhydrophobicity is one of the most interesting. On such surfaces, water droplets maintain a highly spherical shape with contact angles larger than 150°. Superhydrophobicity has vast potential in areas such as self-cleaning, heat transfer, and water purification. Investigations on superhydrophobicity have lasted for a long time with much progress achieved in the past. Previous works found that micro/nano-scale roughnesses on lotus leaves together with wax coating dominate the well-known lotus effect, which endows the leaves with the magic power of self-cleaning to maintain the cleanliness.[1,2] Such a discovery indicates that surface roughness has a crucial effect on fabricating superhydrophobicity, and researchers have since designed diverse rough surfaces to achieve superhydrophobicity.[3–7] Coating a surface using chemicals of very low surface tension is another customary method known as chemical coating, which also leads to superhydrophobicity.[8–20]

Previous approaches to modulate the wetting states are usually achieved by controlling the substrates at the nano/micro-meter scale, with some shortcomings which can be overcome. Surface roughness functions at sizes ranging from a few nanometers to micrometers or larger and the process of fabricating a rough surface is complicated.[21,22] Chemical coating ultimately covers the entire surface, with a full coverage of chemicals and a layer thickness ranging from a few nanometers to several hundred microns.[10,23–25] Therefore, chemical coating processes result in a heavy consumption of time and energy.[8,9]

Theoretically, wetting states are mainly controlled by the fundamental electrostatic and van der Waals interactions between water and the substrate, both of which can be effectively modulated at the atomic scale. This fact points to a theoretical hypothesis that mediating wetting states with atomic scale engineering could be an effective new method for fabricating superhydrophobic surfaces, with significant reductions in the consumption of time and energy.

In the present work, we investigate the wetting states on solid substrates mediated by atomic decoration with silicones. We propose that atomic decoration is a new approach for fabricating superhydrophobic surfaces. As the concentration of silicones increases to a critical partial coverage, the contact angle of water droplets grows significantly to achieve superhydrophobicity. We use molecular dynamics simulations to understand wetting states on a substrate decorated with silicone molecules. The substrate becomes superhydrophobic when the decoration ratio of silicone increases. The analysis reveals that atomic decoration weakens the interaction of substrates with water molecules, evidenced by the decrease in the *effective potential-well depth*. Our results hint at a paradigm shift from macroscopic wetting to atomic-scale wetting control and provide new insights into fabricating superhydrophobic surfaces.

EXPERIMENTAL RESULTS

We have reported a superhydrophobic substrate constructed by employing titanium dioxide (TiO_2) nanoparticles and polydimethylsiloxane (PDMS) under various facile conditions.[26] The crucial factor for superhydrophobicity is that the silicones originating from PDMS cover the superhydrophilic

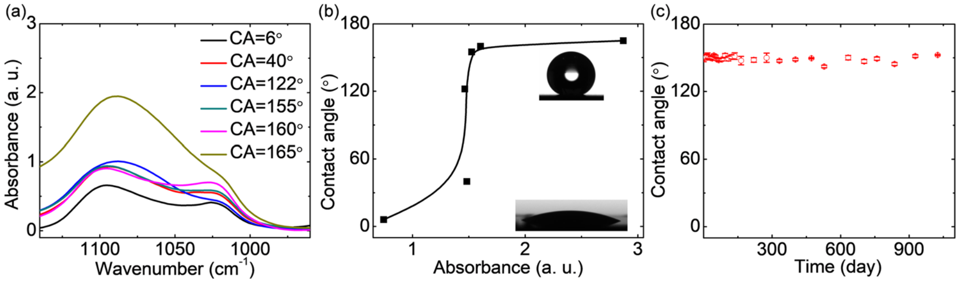

FIG. 1. Infrared (IR) spectrum characterization and wettability of TiO_2/PDMS. (a) IR of the samples with different contact angles (CAs). (b) Contact angle as a function of the sum absorbance of the infrared spectrum at 1027 cm^{-1} and 1090 cm^{-1}. (c) The contact angle remains around 150° tested in the outside environment as a function of time lasting for more than 1000 days.

TiO_2 film (contact angle $< 5°$), favoring a superhydrophilicity-to-superhydrophobicity transition. Here, we modulate the wetting states more precisely by decreasing the intensity of the ultraviolet light and irradiation time (supplementary material). We employ the infrared (IR) spectrum to characterize the concentration of silicone molecules on the surface shown in Fig. 1(a). The sum absorbance intensity of 1027 cm^{-1} and 1090 cm^{-1} is used because both are characteristic peaks of silicone molecules.[27,28] We show the relationship between the contact angle and the IR intensity in Fig. 1(b). As the intensity increases, the contact angle grows and finally leads to a superhydrophobic wetting state. This shows that the concentration of silicone molecule has a positive effect to attain superhydrophobicity.

We further infer that silicone molecules only cover a fraction of surface areas of TiO_2 nanoparticles because the photocatalytic property, active only on clean TiO_2 surfaces, retains after the TiO_2/PDMS film becomes superhydrophobic. This is totally different from the conventional chemical coating approaches, which usually attain a full coverage with typical thicknesses of tens of nanometers to several hundred microns. We define the process of partial covering and patterning of silicone molecules on TiO_2 nanoparticles as "atomic decoration." The "atomic decoration" takes place with a submonolayer coverage and a film thickness of several angstroms, which differs greatly from chemical coating whose thickness is at the micrometer scale.[9,29]

Atomic decoration can be accomplished in a quick and facile way, saving both time and energy, while the other properties of the decorated substrate are well preserved.[26] Besides, the superhydrophobic surface maintains a long lifetime. The contact angle on the surface remains around 150° after more than 1000 days in our samples, operated in the outside environment [Fig. 1(c)]. The flexibility and long lifetime justify the excellent performance of atomic decoration in modulating the macroscopic wetting.

MOLECULAR DYNAMICS SIMULATIONS

To further understand the effects of atomic decoration on macroscopic wetting states, we perform molecular dynamics (MD) simulations to study wetting behaviors on a substrate decorated with silicone molecules.[30–34] We choose silicone molecules because they are the product of PDMS under ultraviolet treatment in our experiment. Simulations of atomic decoration are essentially different from previous works which do not consider atomic-scale roughness and submonolayer decorations.[32–38] Since the chemical composition and surface tension of silicone molecules and the substrate are different, atomic decoration does not produce a chemically pure surface, neither it purely produces the roughness effect. We emphasize that silicone molecules only decorate surfaces partially, rather than coating them entirely to form a uniform film with a finite thickness, which makes atomic decoration different from chemical coating.

Our simulations consider six types of silicone molecules with different lengths. We define the name of silicone molecules according to the number of silicon atoms they contain. For example, a silicone molecule in Fig. 2(a) owning one silicon atom is defined as silicone-1. So follows silicone-*n* with *n* silicon atoms in the molecule.

The decoration ratio is defined based on the separation between adjacent silicone molecules. The ratio 100% corresponds to 7.86 silicones per nm^2 (silicones/nm^2); therefore the surface is fully covered by silicones in this case (see the supplementary material). As the separation becomes larger, we decorate the substrate at different ratios. We consider

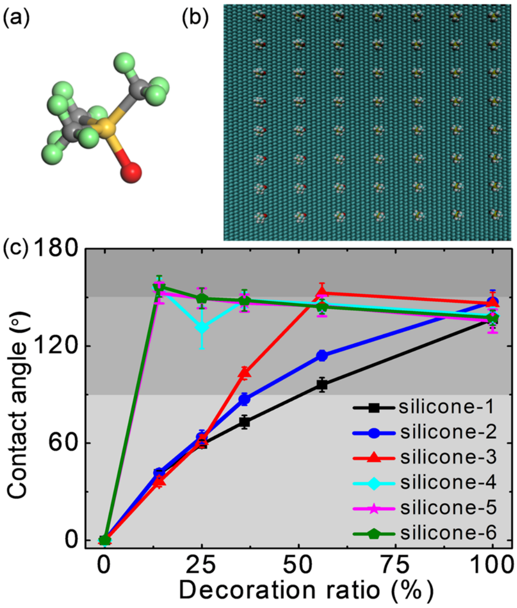

FIG. 2. MD simulations of water on the atomically decorated substrate. (a) Molecular structure of the silicone-1 molecule (with one silicon atom). The oxygen atom is red, the silicon atom is yellow, the carbon atom is gray, and the hydrogen atom is green. (b) Top view of the substrate decorated with silicone-1 at a decoration ratio of 14%. (c) Contact angle on the decorated substrate as a function of decoration ratio using different silicone molecules.

the decoration with the ratios of 0 (no silicone), 14% (1.10 silicones/nm^2), 25% (1.96 silicones/nm^2), 36% (2.83 silicones/nm^2), 56% (4.42 silicones/nm^2), and 100%. Figure 2(b) is the top-view image of a substrate decorated with silicone-1 at a partial coverage of 14%.

The wetting states simulated on substrate decorated with silicones are shown in Fig. 2(c). The contact angle on the substrate decorated with silicone-1 increases from 41.1° at the decoration ratio of 14% to 96.1° at 56% and reaches a maximum of 136.5° at a full coverage of 100%. Other silicone molecules also yield a hydrophobic or even superhydrophobic wetting state when their coverage increases. Transitions of hydrophilicity to hydrophobicity by silicone decoration in MD simulations are in good agreement with above experimental results.

We define the transition ratio to represent the capacity of transforming a hydrophilic substrate into a hydrophobic one quantitatively (see the supplementary material). It is obvious that the transition ratio is related to the length of silicone molecules. We see from Fig. 3 that the transition ratio decreases as the silicone length increases, and approaches a constant. The critical ratio is 56% for the silicone length of 0.41 nm, 40% for the length of 0.72 nm, 33% for the length of 1.03 nm, and decreases sharply to as small as ∼8% for silicone molecules whose length ≥1.34 nm. This suggests that silicone-decorated substrates with a silicone length of only several angstroms could introduce superhydrophobic wetting. Therefore, atomic decoration is a very effective and reliable method for fabricating superhydrophobic surfaces.

To understand the effectiveness and underlying mechanism of atomic decoration, we investigate the total interaction energy between water molecules and the substrate using the Lennard-Jones (L-J) model potential,

$$U(r) = \sum_{i=1}^{N_{spot}} \sum_{j=1}^{N_{atom}} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \qquad (1)$$

In Eq. (1), N_{spot} is the number of spots where water resides in a flat level above the substrate, N_{atom} is the number of atoms in substrate, ε and σ are the L-J parameters of the atom, and r is the distance from the atoms to the spots. The spots are possible sites where the water molecule stays. Equation (1) represents interactions between the atomic decorated substrate and water above it.

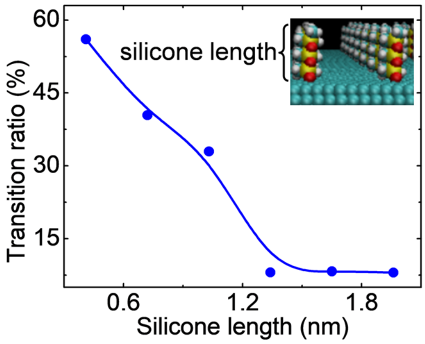

FIG. 3. Transition ratio as a function of the molecular length of silicone molecules (Inset: side-view image of the atomic-decorated substrate).

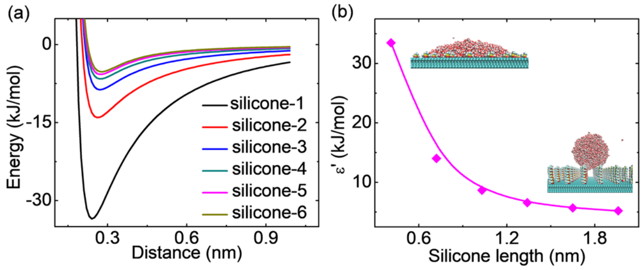

FIG. 4. Atomic decoration mechanism. (a) Total L-J energy of the substrates decorated with different silicone molecules at a ratio of 14%. (b) The *effective potential-well depth* (ε') as a function of silicone length. Insets: snapshots of the side-view images of water droplets on the substrates decorated with silicone-1 and silicone-6, both at the decoration ratio of 14%.

Figure 4(a) shows the total interaction energy of substrates decorated with different silicones at a ratio of 14%. The total L-J energy has the same form as the L-J potential between two atoms. We fit the curve to derive *effective zero-potential distance* σ' and *effective potential-well depth* ε' to describe the interaction of the substrate with the water droplet. Change of σ' is negligible, while ε' varies strikingly. We show how ε' changes with respect to silicone molecule length in Fig. 4(b). As silicone length changes from 0.41 nm to 1.96 nm, ε' decreases sharply from 33.5 kJ/mol and approaches a constant of 5.2 kJ/mol. The contact angle increases to superhydrophobic wetting sates as shown by the inset images in Fig. 4(b) when ε' decreases. In addition to the silicone length, the increasing decoration ratio also makes the small ε' and then yields superhydrophobic wetting states (see the supplementary material).

The essence of atomic decoration lies in the dramatic decrease in the *effective potential-well depth* with a submonolayer coverage of atoms/molecules. The atom decoration is very efficient to significantly weaken the interaction between the solid surface and water droplet, thus turning a hydrophilic surface into a superhydrophobic one, as the decoration ratio and silicone length increase. We note that the atomic-scale roughness in atomic decoration is conceptually different with surface roughnesses at nano- and micro-scales, where water cannot penetrate the atomic-scale empty space in the former case, thanks to steric hindrance between molecules, but water contact closely with the substrate in the latter.

CONCLUSION

We show that atomic decoration modulates macroscopic wetting states by transforming a hydrophilic surface into a superhydrophobic one in both experiments and simulations. Atomic decoration is low cost in terms of time and energy. The resulting superhydrophobic surface maintains a long lifetime of more than 1000 days tested so far. MD simulations show that the decoration ratio to achieve superhydrophobicity can be as small as ∼8%. Atomic decoration differs from chemical coating in partially covering a substrate and functions at the atomic scale (typical interaction length: several angstroms). We propose a model based on interaction energies between water and decorated substrates to explain the effectiveness of the atomic decoration approach. Silicone molecules decrease the *effective potential-well depth* and thus weaken the water-substrate interaction, favoring superhydrophobicity. Our results are significant in terms of pushing research activities on macroscopic wetting states to the ultimate size limit of atomic scales, providing an economic low-consumption approach to fabricate long-lived superhydrophobic surfaces.

METHODS

Experiments

The samples in our experiments are fabricated in the following steps. First, the PDMS is spin-coated on the copper foil or other substrates, then a droplet of TiO_2 (P25, Shanghai Evonik) suspension in ethanol is put onto PDMS films. The ultraviolet source is placed above to irradiate the sample. More experimental details can be found in Ref. 26 and the supplementary material.

MD simulations

MD simulations are used to study water wetting states on a hydrophilic substrate decorated with silicone molecules. The substrate is flat and contains 20 568 atoms. Silicone molecule contains 14, 24, 34, 44, 54, and 64 atoms, respectively. Therefore, the total atom number of the substrate varies according to different molecule types and absorption ratios. The dimension of the system is 15.336 nm × 15.052 nm × 15.000 nm with three-dimensional periodic boundary conditions used. Initially a cubic water box with a size of 5 nm × 5 nm × 5 nm containing 3916 water molecules was put on the surface with a distance of 0.5 nm to the surface. The L-J parameters for atoms in substrate are $\sigma_{\mathrm{Sub}} = 0.3214$ nm and $\varepsilon_{\mathrm{Sub}} = 1.8000$ kJ/mol, in order to make a superhydrophilic substrate. Parameters for Si are $\sigma_{\mathrm{Si}} = 0.3400$ nm and $\varepsilon_{\mathrm{Si}} = 0.5336$ kJ/mol,[39] for C atom $\sigma_{\mathrm{C}} = 0.3635$ nm and $\varepsilon_{\mathrm{C}} = 0.3264$ kJ/mol, for O atom $\sigma_{\mathrm{O}} = 0.3029$ nm and $\varepsilon_{\mathrm{O}} = 0.5021$ kJ/mol, for H atom $\sigma_{\mathrm{H}} = 0.2388$ nm and $\varepsilon_{\mathrm{H}} = 0.1004$ kJ/mol, and for O atom in water $\sigma_{\mathrm{OW}} = 0.3166$ nm and $\varepsilon_{\mathrm{OW}} = 0.6502$ kJ/mol, respectively. The simple point-charge (SPC) water model is used.[40] Cutoffs for van der Waals interactions are 1 nm, and Ewald summation is used for electrostatic interactions, the same as before.[31,34] The first stage of simulation relaxes the system to an equilibrium state and then the simulations are performed in the canonical ensemble (NVT ensemble) with a constant particle number, temperature, and volume at 300 K. The time step is 2 fs in all simulations. The second stage lasts for 5 ns, and the trajectory in the final 1 ns is used for data collection. All simulations are performed by Gromacs.[41]

SUPPLEMENTARY MATERIAL

See supplementary material for methods of modulating wettability of the TiO_2/PDMS system, original IR spectrum, characterization of surface roughness. Also included are the decoration ratio, transition ratio, and calculation of potential of mean force. We also show the L-J potential of the undecorated surface, the relationship of L-J, and *effective potential well-depth* as a function of decoration ratio.

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