

Reversible Liquid Adhesion Switching of Superamphiphobic Pd-Decorated Ag Dendrites via Gas-Induced Structural Changes

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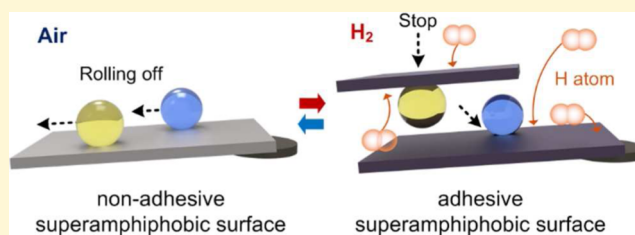
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S Supporting Information

ABSTRACT: Adhesion control of various liquid droplets on a liquid-repellent surface is a fundamental technique in novel open channel microfluidic systems. Herein, we demonstrate reversible liquid droplet adhesion switching on superamphiphobic Pd-decorated Ag dendrites (Pd/Ag dendrites). Although adhesion between liquids and the superamphiphobic surfaces was extremely low under ambient air, high adhesion was instantly achieved by exposure of the dendrites to 8% hydrogen gas. Transition from low to high adhesion and the reverse case were successfully repeated more than 10 times by switching from atmospheric ambient air to 8% hydrogen gas. This is the first technique that allows real-time reversible adhesion change with various liquid droplets to a surface using gas-induced structural changes and can potentially be used to realize various functions for droplet-based microfluidics.



1. INTRODUCTION

Super-repellent surfaces with special adhesion, which are low-adhesive or high-adhesive with respect to liquid, have recently attracted a great deal of attention because of their various applications such as self-cleaning surfaces¹ and anticorrosion coatings,² their ability to provide no-loss droplet transfer,³ and their potential applications in droplet-based open channel microfluidic devices.^{4,5} In particular, reversible switching of the adhesion of super-repellent surfaces, which provides controllability of the droplets, such as instant moving or stopping at a desired moment, is crucial for realization of droplet-based open channel microfluidics. Droplet-based open channel microfluidic devices have many advantages compared to conventional microfluidic devices, such as extremely weak interaction between the surfaces and droplet sample, the simple design of the system, and no loss of liquid droplets during manipulation of the sample. Many researchers have developed methods for obtaining super-water-repellent surfaces with reversible adhesion switching by precisely tuning morphologies or surface chemistry using external stimuli such as light,⁶ pH,⁷ electric field,⁸ and temperature.⁹ Meanwhile, adhesion changing between the water droplet and special surface such as a lubricant-infused porous surface also has been reported to achieve more efficient droplet controllability.¹⁰ In our previous report, we demonstrated reversible adhesion switching of Pd-sputtered superhydrophobic surfaces using gas-stimulated morphological changes.^{11,12} However, the methods described

above cannot be applied to the liquid droplets with low surface tension, such as oil and organic solvents.

Superamphiphobic surfaces, which are highly repellent not only to water but also to other liquid types like oil, have a complicated morphology and very low surface tension.^{13–15} Most studies of superamphiphobic surfaces have concentrated only on developing them through simple fabrication steps, including conventional photolithography of silicon wafers,¹⁶ electrospinning,¹⁷ and spray coating with fluorinating materials.¹⁸ Recently, a few research groups have developed superamphiphobic surfaces with reversibly tunable liquid adhesion properties by subtly changing surface roughness and chemistry. Zhou et al. controlled adhesion between liquid droplets and a fluorinated anodized Ti superamphiphobic surface by tailoring the surface energy by alternate treatments with ultraviolet light and annealing.¹⁹ Similarly, Li et al. tuned the adhesion of an Al superamphiphobic surface by plasma treatment, which increased the surface energy through oxidation and defluorination of the fluorinated surface.²⁰ However, these simple methods could affect droplets on the superamphiphobic surfaces, because these droplets would also be exposed to plasma, ultraviolet light, and high temperatures, which may make these methods inappropriate for biorelated

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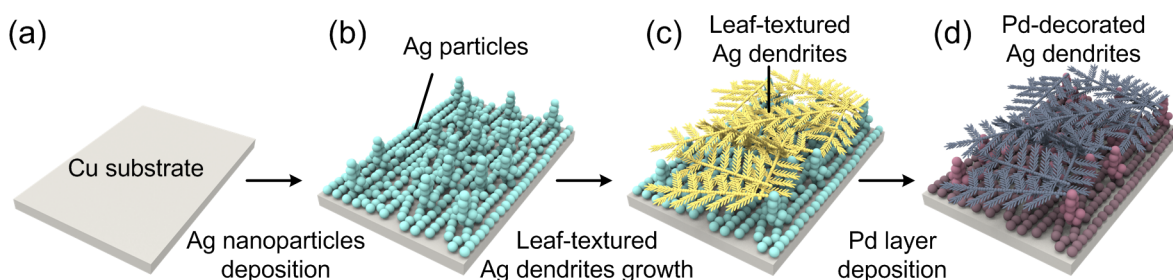


Figure 1. Schematics of fabrication steps for Pd/Ag dendrite superamphiphobic surfaces. (a) Bare Cu substrate. (b) Nucleation and deposition of Ag particles on the bare Cu surface after immersion of the Cu substrate in a AgNO_3 solution. (c) Leaf-textured Ag dendrite growth on Ag particles with increasing immersion time (t_{Ag}) in a AgNO_3 solution. (d) Uniform deposition of Pd particles on the Ag dendrites without destruction of the Ag dendrites.

microfluidics. Additionally, annealing or recoating of the fluorine materials was required to recover low-adhesive superamphiphobic surfaces, which is a potential technical barrier to the realization of a real-time droplet manipulation system. For reversible oil droplet adhesion control, morphological or chemical modulation of the surface has to be implemented. However, the control of surface chemistry could cause full wetting of oil droplets on a rough surface during the transition because of the low surface tension of liquids. Therefore, the development of a technique that allows a delicate morphological change of a rough surface is required.

Here, we developed Pd-decorated Ag dendrite (Pd/Ag dendrite) superamphiphobic surfaces with adhesive properties that could be reversibly changed by gas-stimulated morphological changes. A low-adhesive superamphiphobic surface was achieved by a facile, sequential, electroless galvanic replacement reaction between Ag and Cu, followed by deposition of Pd on the Ag dendritic structures. A 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT) coating of the Pd/Ag dendrite yielded a low-adhesive superamphiphobic surface for various liquids from water to *n*-hexadecane (HD). Adhesion of the droplets to the superamphiphobic surfaces was dramatically increased by exposing the surfaces to 8% H_2 gas, because the morphology of Pd on the Ag dendrites changed in response to absorption of hydrogen atoms. We confirmed that the increase in adhesion force was much higher for lower-surface tension liquids than for higher-surface tension liquids because of the high level of infiltration of the expanded Pd/Ag dendrites by the lower-surface tension liquids. Reversible adhesion of superamphiphobic surfaces was observed in response to repeated switching between air and ambient hydrogen; switching was successfully repeated more than 10 times without any liquid residue. Superamphiphobic surfaces with the ability to switch their adhesion properties under alternative ambient gases can potentially be used for droplet manipulation, such as droplet transportation, selection, and separation, in next-generation droplet-based microfluidic devices.

2. EXPERIMENTAL SECTION

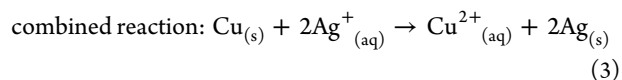
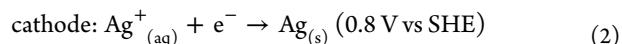
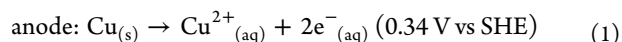
2.1. Fabrication of a Superamphiphobic Surface. A 1.5 cm $\times$ 1.5 cm Cu foil was subsequently cleaned with acetone, isopropyl alcohol (IPA), and deionized water to remove contaminants. The cleaned Cu foil was dipped into CH_3COOH (20%, Ducksan Pure Chemicals Co.) for 2 h to eliminate the copper oxide and remove the residue remaining on the Cu surface. After being cleaned, the substrate was immersed in an aqueous solution of 6 mM AgNO_3 (99%, Sigma-Aldrich Co.); the Ag^+ ions in the solution were reduced and deposited on the Cu foil by electroless galvanic replacement reaction.²¹ Then, the Ag-deposited Cu foil was added to 1 mM PdCl_2 (99.9%, Sigma-

Aldrich Co.) dissolved in a 2% HCl (35%, Ducksan Pure Chemicals Co.) aqueous solution. The PdCl_2 was converted into PdCl_4^{2-} ion in HCl aqueous solutions, and Pd particles could be grown on Ag/Cu foil via the same galvanic cell reaction mechanism. To achieve the low surface energy, the as-prepared Pd/Ag dendrite/Cu foil was decorated by being immersed in a 1 mM ethanol solution of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT, 97%, Sigma-Aldrich Co.) for 1 h and baked at 120 $^\circ\text{C}$ for 30 min.

2.2. Characterization. Surface morphologies and EDS elemental mapping were performed on a JEOL JSM-7001F field emission scanning electron microscope (FE-SEM) and a Park System XE-150 atomic force microscope (AFM). The coverage of leaf structure was measured by analysis of SEM images (90 $\times$ magnification) using ImageJ [National Institutes of Health (<http://rsb.info.nih.gov/ij/>)]. The contact angles (CAs) were observed using a CA measurement instrument (Phoenix 300, SEO Co. Ltd.) using the ~ 7 μL droplets for each liquid; 8% H_2 gas was directly blown onto the surface using a tube connected with an 8% H_2 gas cylinder equipped with a valve for gas injection. The resistance changes were measured using a Keithley 2400 source measurement unit connected to two electrical wires using a feedthrough, and the bias voltage was 10 mV.

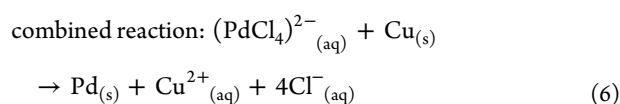
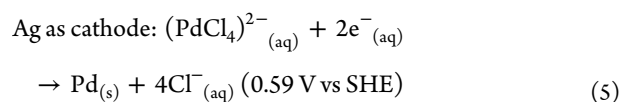
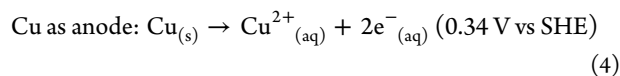
3. RESULTS AND DISCUSSION

Figure 1 shows schematically illustrated fabrication steps of Pd/Ag dendrite structure on a Cu substrate. Ag and Pd deposition was conducted by electroless galvanic replacement reaction. When the bare Cu substrate (Figure 1a) was immersed in a AgNO_3 aqueous solution, a Ag micro/nanoparticle layer formed spontaneously on the flat Cu substrate because of the different electrochemical reactivity of Ag and Cu (Figure 1b). Because Ag ions have a reduction potential [$E^0 = 0.80$ V, relative to the standard hydrogen electrode (SHE)] higher than that of Cu ions ($E^0 = 0.34$ V), Ag particles can be reduced and deposited from Ag ions when provided with electrons from the bulk Cu substrate.²² This electroless galvanic replacement reaction can be written as follows.



As the Ag deposition time (t_{Ag}) increased, Ag particles aggregated and leaf-textured Ag dendrites formed. The entire galvanic replacement reaction complied with reduction–nucleation–growth steps, especially Ag on the Cu substrate, which underwent additional branching growth steps.²³ As illustrated in Figure 1c, the leaf-textured Ag dendrites eventually covered the entire Ag particle/Cu substrate by

aggregation and branching. A Pd layer was subsequently deposited on the Ag dendrite/Cu substrate without destruction of the Ag structures fabricated in the prior stage via the same electroless galvanic replacement reaction. When PdCl_2 was dissolved in a 2% HCl aqueous solution, PdCl_2 was converted to PdCl_4^{2-} ions, which were then reduced to Pd on the Ag dendrite/Cu substrate. In this case, Cu atoms were oxidized as an anode, and conversely, Ag dendrites acted as a cathode substrate that did not participate in the whole reaction, as shown in the following equations.²⁴



Consequently, Pd atoms deposited on the Ag dendrite/Cu substrate formed as aggregated particles, and the Ag dendrite double-layer texture was maintained, providing rough surfaces. Therefore, a superamphiphobic surface was fabricated in a simple manner through solution-based galvanic replacement reactions.

Figure 2 shows typical top and tilted view SEM images of Ag dendrite-textured surfaces according to t_{Ag} . As shown in Figure 2a, Ag particles were deposited on the Cu substrate after dipping the Cu substrate in a AgNO_3 aqueous solution for 5 min. Ag particles with various sizes ranging from 1 to 2 nm to a few micrometers were widely distributed on the Cu surfaces because of the reduction–nucleation–growth step of the galvanic replacement reaction. Leaf-textured Ag dendrites could not be detected on the Cu substrate at a t_{Ag} of 5 min. As t_{Ag} increased, nucleated Ag particles grew more actively at particular sites that were energetically favorable,^{22,25} and leaf-textured Ag dendrites started to form because of repeated Ag ion reduction on Ag particles at a deposition time of 20 min (Figure 2b). Figure 2c shows that leaf-textured Ag dendrites entirely covered the surface of the Cu substrate at a t_{Ag} of 100 min. Ag dendrites had a main trunk and branches with nanosized particles, and branches were parallel to each other and had a morphology similar to that of their main trunks. The tilted view of Pd/Ag dendrites provided in Figure 2d shows that Ag leaf-textured dendrites hung in the air with voids under the leaves, which are regarded as numerous re-entrant sites. Figure 2e shows the coverage of leaf-textured Ag dendrites as a function of t_{Ag} . There were no leaf-textured Ag dendrites at $t_{\text{Ag}} = 5$ min, corresponding to a surface coverage of 0%. Coverage by leaf-textured Ag dendrites increased as t_{Ag} increased, and coverage was greater than 73% after 100 min. When the t_{Ag} is >100 min, the leaf coverage was increased and the surface was fully covered with Ag dendrites. However, the Ag ions were gradually reduced on the as-grown Ag leaf texture after 100 min; therefore, the number of nanopores between leaves was decreased. The widened leaf surface and small nanopores lead to a smooth surface morphology as shown in Figure S1 of the Supporting Information. Pd layer deposition was conducted on the as-prepared Ag dendrite substrates using the electroless galvanic replacement reaction. Figure S2 of the Supporting

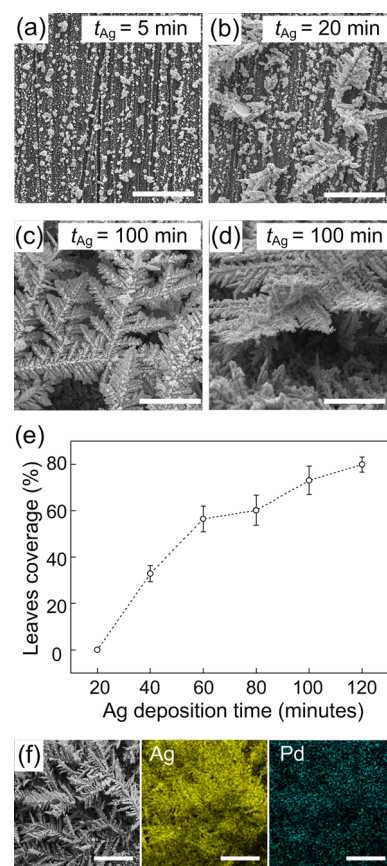


Figure 2. (a–c) Top views of FE-SEM images of Ag dendrites grown as a function of increasing t_{Ag} . (a) Micro/nano-Ag particle nucleation and deposition at a t_{Ag} of 5 min. (b) Leaf-textured Ag dendrite growth from Ag particles deposited after a t_{Ag} of 20 min. (c) Fully covered leaf-textured Ag dendrites on Ag particles deposited on the Cu substrate. (d) Tilted view (tilting angle of 40°) of a FE-SEM image of Ag dendrites (scale bar of 10 μm). (e) Leaf-textured Ag dendrite coverage as a function of t_{Ag} . (f) EDS images of Pd/Ag dendrites (scale bar of 25 μm).

Information shows the leaf-textured Ag dendritic structures before and after Pd layer deposition. Leaf-textured Ag dendrite structure without a Pd layer comprised Ag leaves covering Ag particles (Figure S2a of the Supporting Information). In contrast, after Pd layer coating, some Pd particles were deposited on the leaf-textured Ag dendrites (Figure S2b of the Supporting Information). Notably, leaf-textured Ag dendrites remained intact after the Pd deposition process. The magnified SEM images in Figure S2 of the Supporting Information and the AFM image in Figure S3 of the Supporting Information show morphological changes of the leaf-textured Ag dendrites before and after deposition of Pd; the Ag dendrites were well-decorated with Pd particles. The Ag dendritic structure after Pd layer deposition was more nanotextured and had greater roughness because it was covered by aggregated Pd nanoparticles. To confirm the existence of a Pd layer on the Ag dendrites, energy-dispersive spectroscopy (EDS) elemental mapping was performed as shown in Figure 2e. EDS mapping confirmed that the Ag and Pd atoms were distributed evenly on the surface.

By using a simple dip coating method, a PFDT coating on the as-prepared Pd/Ag dendrites was achieved, resulting in a superamphiphobic surface. Figure 3a shows the relation between the t_{Ag} and CAs for four types of liquids with different

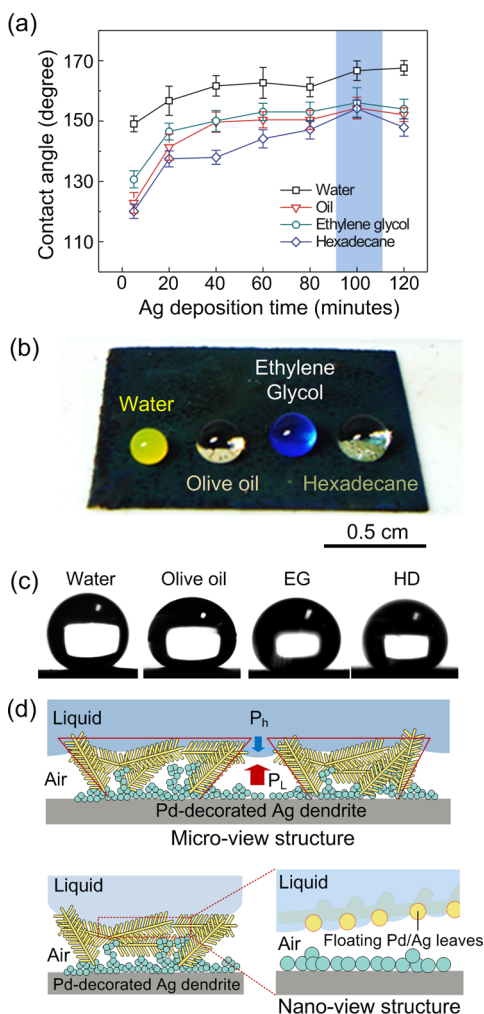


Figure 3. Superamphiphobicity of the Pd/Ag dendrite surface. (a) CA for each liquid at a different t_{Ag} . (b) Photographic image showing the high CAs of water, olive oil, EG, and HD droplets on the Pd/Ag dendrite superamphiphobic surface. (c) Optical images of liquid droplets with a volume of 7 μ L on the Pd/Ag dendrite superamphiphobic surface. (d) Illustration of the principle of superamphiphobicity of the Pd/Ag dendrite surfaces.

surface tensions. Different t_{Ag} values were used, but the Pd deposition time was held constant at 100 min. The apparent CA of each liquid increased proportionally with the increasing t_{Ag} , and it might be significantly attributed to the roughness of the substrate. In the case of water (surface tension of ~ 72.8 mN/m), the CA was greater than 150° on the surface at a t_{Ag} of 5 min. After that, the water CA increased moderately to $>160^\circ$ as time increased. In contrast, for liquids with a surface tension lower than that of water [ethylene glycol (EG), olive oil, and HD], the CAs at a t_{Ag} of 5 min were much lower than 150° , and the CA values showed a linear relationship to the surface tension of the liquid. The CAs of all liquids increased gradually with an increasing t_{Ag} , and the CA of every liquid was greater than 150° at a t_{Ag} of ≥ 100 min. Panels b and c of Figure 3 are photographic images of 7 μ L of water, EG, olive oil, and HD droplets with CAs of $>150^\circ$. Furthermore, a low sliding angle ($<10^\circ$ for all liquids) was observed on the Pd/Ag dendrite superamphiphobic surfaces [$t_{Ag} = 100$ min and Pd deposition time (t_{Pd}) of 100 min]. The relation between t_{Ag} and CAs in Figure 3a was comparable with that shown in Figure 2e, which exhibited a dependency between t_{Ag} and Ag leaf coverage. An increase in t_{Ag} was related to increases in both the amount of Ag leaf coverage and the CA. These relations indicated a dependency between surface coverage of leaf-textured Ag dendrites and the superamphiphobicity of the surfaces.

Superamphiphobicity of our surfaces can be ascribed to two factors: microscale overhang-like structures, and hierarchical structures with a large number of nanoscale air cavities. Figure 3d illustrates the schematics of micro- and nanostructure cross views of the Pd/Ag dendrite surface. In the microstructure view, the leaf-textured Ag dendrites originating from the Ag particles had greater growth on the upper side and comparatively meager bottoms; this dendrite morphology can be schematically depicted as a microscale overhang-like structure. The distinctive microscale overhang-like layer composed of leaf-textured Ag dendrites and Ag particles was sufficiently rough to achieve superamphiphobicity as follows.^{26,27} When a liquid with a low surface tension sits on an overhang structure, the meniscus between the liquid and cavities has a convex shape. The direction of the Laplace pressure (P_L) at the interfaces is upward and competes with hydrostatic pressure (P_H) because of the gravity of the liquid

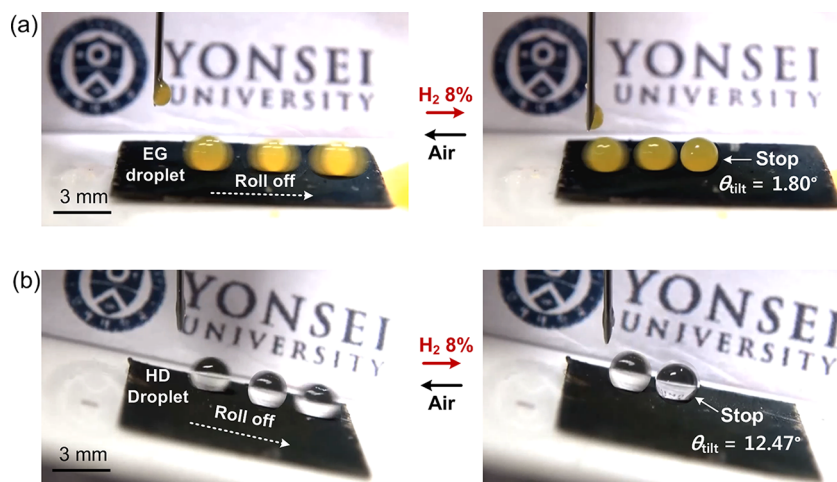


Figure 4. Photographic images of a 7 μ L (a) EG droplet and (b) HD droplet on the Pd/Ag dendrite superamphiphobic surface under atmospheric ambient conditions (left) and 8% ambient H_2 (right).

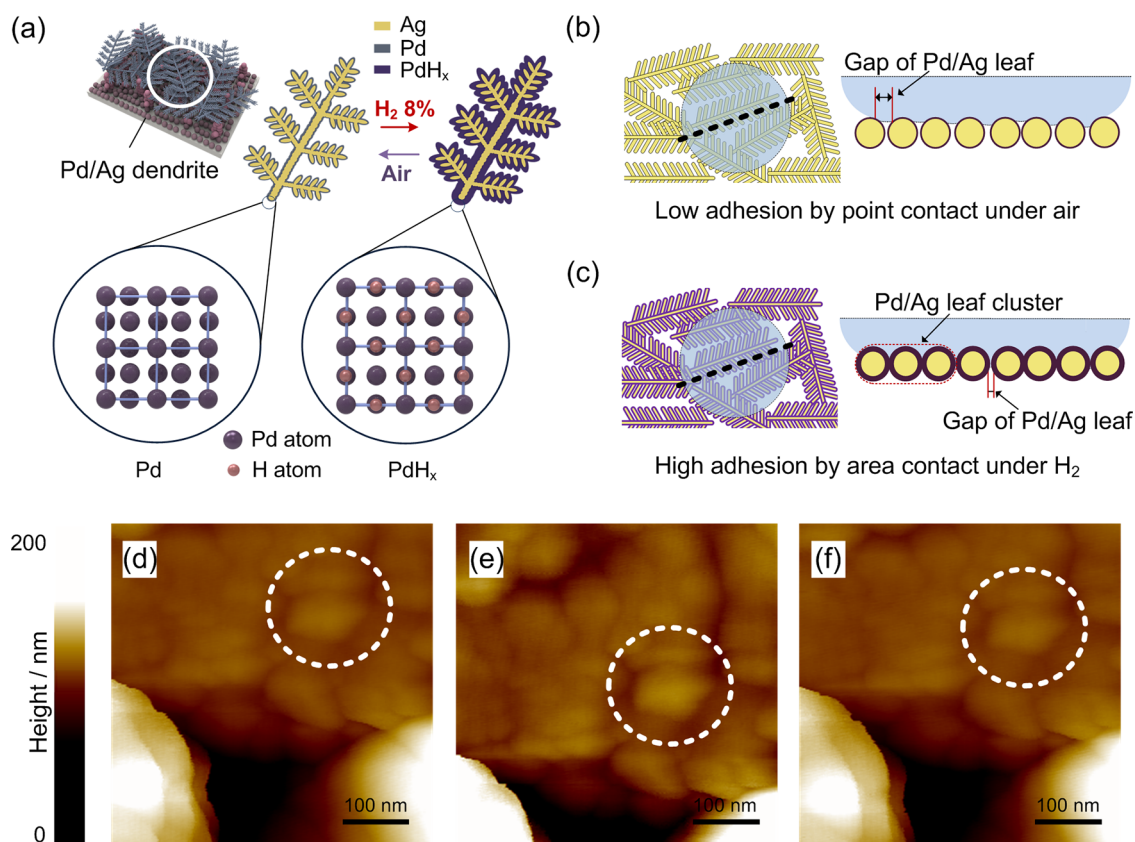


Figure 5. (a) Schematic illustration of the volume expansion of the Pd layer on leaf-textured Ag dendrites that contact the liquid droplet. Schematic illustration for explaining the change in adhesion between the liquid and the surface: leaf-textured Pd/Ag dendrites under (b) ambient air and (c) ambient H₂. In situ AFM characterization of Pd/Ag dendrites under different gas ambient conditions: Pd/Ag dendrite surface under (d) ambient air, (e) ambient H₂ gas, and (f) re-exposed air ambient. Here, the white dotted line circle denotes the same position of Pd/Ag dendrites.

droplet. P_L in the opposite direction to P_H can act as an energy barrier, prohibiting liquid infiltration and wetting of surfaces. In addition, in the nanostructure view, the hierarchical structure of Pd/Ag dendrites and their cavities could also contribute to the superamphiphobicity of the surfaces. Numerous nanoscale cavities of leaf-textured Ag dendrites and cavities between Pd particles on the Ag dendrites created numerous air pockets under the liquid that sat on the Pd/Ag dendrite surfaces, as explained by the Cassie–Baxter relation:^{28,29}

$$\cos \theta_c^* = -1 + f(\cos \theta + 1) \quad (7)$$

where θ_c^* is the apparent CA on rough surfaces, f is the ratio of the actual area in contact with the droplet to the total area of the rough surface, and θ is Young's angle on the flat surface. The Cassie–Baxter relation showed that contact liquid droplets on the rough surfaces could not easily permeate the surfaces because of air pockets, resulting in a small contact area between the liquid and the surface and an extremely high CA for various liquids. Similarly, because of both the microscale overhang structure and the nanocavities of dendrites, the Pd/Ag dendrite surfaces could maintain Cassie–Baxter states for various liquids with very low surface tensions.³⁰ Increasing the t_{Ag} from 100 to 120 min resulted in slight decrease in CA because of the continuous growth of Ag dendrites on the both particles and the leaf layer, which decreased not only the height of the micro-overhang structure but also the amount of cavities on the surfaces, as shown in Figure S1 of the Supporting Information.

Figure 4 shows the movement of a 7 μ L droplet under two different atmospheric conditions to demonstrate changes in the

adhesion properties of the Pd/Ag dendrite superamphiphobic surfaces ($t_{Ag} = 100$ min, and $t_{Pd} = 100$ min). We used 8% H₂ gas to switch the surrounding ambient atmosphere. Figure 4a shows time-sequential photographs that show EG droplet motion on a superamphiphobic surface with a tilting angle of 1.8° under air and 8% ambient H₂. Under ambient air, the EG droplet easily rolled off the superamphiphobic surface with no adhesion because of gravity. However, after the surface had been exposed to 8% H₂ gas for 30 s, the adhesive properties of the superamphiphobic surface changed, and the EG droplet was pinned to the middle of the surface. The HD droplet behaved in a manner similar to that of the EG droplet, but the HD droplet was pinned at an even greater tilted angle of 12.47° under ambient H₂. When the sticky surface was again exposed to ambient air, the roll-off property was recovered within 1 min (see the Supporting Information videos for more details).

This switching in adhesion properties can be explained by the reaction between Pd on the Pd/Ag dendrites and hydrogen atoms. Hydrogen atoms are highly soluble in Pd, resulting in the formation of palladium hydride (PdH_x) when Pd is exposed to ambient H₂. Pd deposited by the galvanic replacement reaction has a face-centered-cubic (fcc) structure. Exposure of fcc Pd to hydrogen atoms results in the formation of PdH_x, because the hydrogen atoms permeate and settle into the octahedral interstitial sites of the Pd fcc structure under ambient hydrogen.³¹ In PdH_x states, the lattice distance between Pd atoms increases from ~ 3.90 to ~ 4.04 Å while undergoing phase transition of PdH_x, which causes a volumetric expansion of the Pd layer with a maximum of 0.7 Å³ per H

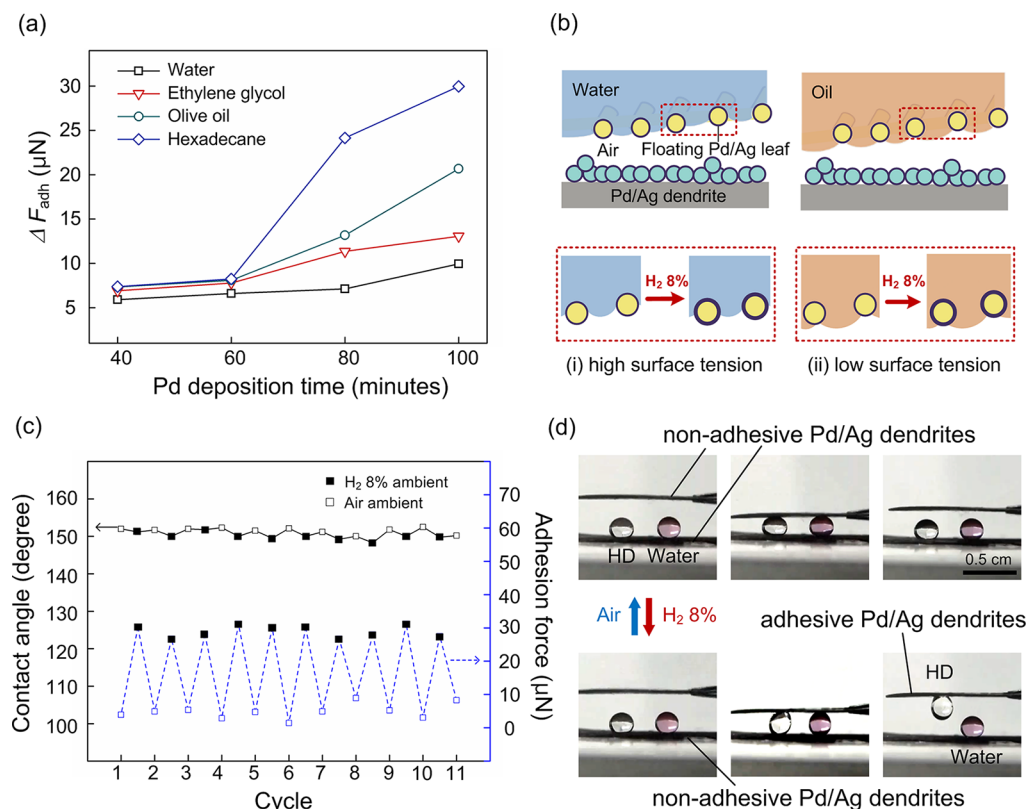


Figure 6. (a) ΔF_{adh} of the Pd/Ag dendrite superamphiphobic surface for individual liquids with different t_{Pd} values after H₂ exposure. (b) Schematic illustration of the relation between the Pd/Ag dendrite superamphiphobic surface and liquids with large or small surfaces. (c) Reversible HD adhesion switching of the Pd/Ag dendrite surface in response to alternative atmospheres (air and 8% H₂). (d) Photographic images of selection of HD droplets using the Pd/Ag dendrite superamphiphobic surface after H₂ exposure.

atom on the Pd/Ag dendrite substrate.³² In our study, after ambient H₂ was broken, the H atoms desorbed from the Pd layer by diffusion, resulting in a reversible Pd swelling/contracting process. Figure 5a illustrates the mechanism of surface morphological changes of the Pd/Ag dendrite substrate in response to H₂ gas exposure. Volumetric expansion of the Pd layer on our substrate enlarged the top area of the Pd/Ag leaf-textured dendrites, which was in contact with the liquid droplet, thereby increasing the contact area between the liquid and the substrate. This subtle change in contact area under ambient H₂ resulted in a force that pinned the droplet to the substrate. The droplet mostly in contact the Pd/Ag leaf-textured dendrites cannot penetrate into the bottom of structure because of the low surface energy of the PFDT coating and robust nanoporosity of the structure. Here, the liquid sitting on the Pd/Ag dendrites could be regarded as the point of contact under ambient air, as shown in Figure 5b. After H₂ exposure, the gap distance was reduced by the volumetric expanded Pd layer. As shown in Figure 5c, some Pd/Ag leaves made a cluster by making contact with another adjacent Pd/Ag leaf, which resulted in the contact area between the solid and liquid. This contact area leads to an increase in adhesion force between the surface and liquid by a continuous three-phase (solid–air–liquid) contact line.³³ Because hydrogen atoms absorbed in the Pd lattice scatter conducting electrons and increase the resistance of Pd surfaces, we used resistance measurements of Pd/Ag dendrites to indirectly confirm that volumetric expansion of Pd had occurred.^{34,35} Figure S4 of the Supporting Information shows the resistance changes of Pd/Ag dendrites in response to switching ambient gas. The resistance was higher

under ambient H₂ than under ambient air. This observation confirmed that H atoms underwent an absorption–desorption process on the Pd/Ag dendrite surfaces, resulting in reversible volume changes. The morphological change in Pd/Ag leaves was also demonstrated by using in situ AFM characterization under alternative atmospheric conditions. The scanning size of AFM images was 0.25 $\mu\text{m} \times 0.25 \mu\text{m}$. Figure 5d displays the Pd/Ag leaves in ambient air. After H₂ gas had been blown into the AFM chamber, the observed position of Pd/Ag leaves was moved downward as shown in Figure 5e. The moving of the Pd/Ag leaves could be contributed to the omnidirectionally volumetric-expanded Pd layer by H₂ gas. The Pd/Ag layer pushed each other, leading to the moving of the captured image. The position of the AFM image in Figure 5f could be recovered by desorption of hydrogen, which showed the reversible morphological change of the Pd/Ag layer in an alternative ambient atmosphere. The adhesion changes of the liquid droplet were not observed on either flat Pd surface without Ag dendrites or a Ag dendrite surface without a Pd layer. The Pd flat surface could not develop superamphiphobicity as shown in Figure S5 of the Supporting Information. The Ag dendrites had higher CAs of all liquids as shown in Figure S6 of the Supporting Information but did not represent pinning behaviors under ambient H₂. Little difference between CAs in air and 8% H₂ showed that both a flat Pd surface and Ag dendrites were not modified morphologically and chemically by a hydrogen atom.

The increase in liquid adhesion force (ΔF_{adh}) depends on the liquid surface tension. To characterize each adhesion force (F_{adh}) and calculate the ΔF_{adh} of the Pd/Ag dendrites for

various liquid droplets, we measured the critical liquid sliding angle before and after H_2 exposure (see details in Figure S7 and the Supporting Information). Figure 6a shows the ΔF_{adh} of each liquid droplet after exposure of the Pd/Ag dendrite surfaces with different t_{Pd} values to H_2 gas. The F_{adh} of the H_2 -exposed surface was larger than that of the air-exposed surface. ΔF_{adh} for all liquids was proportional to t_{Pd} , with a higher t_{Pd} indicating deposition of a thicker Pd layer. These results are plausible, because a thicker Pd layer could potentially undergo greater volumetric expansion than a thinner Pd layer, thereby increasing the pinning force between the liquid droplet and Pd/Ag dendrite surface by increasing the contact area between them. When t_{Pd} was 100 min, the 7 μ L HD droplet was pinned to the surface even when the surface was turned upside down, and the measured adhesion force under ambient H_2 was 31.8 μ N. ΔF_{adh} was higher for liquids with a lower surface tension like HD (27.5 mN/m) than for water (72.8 mN/m). We attributed the liquid surface tension dependency of ΔF_{adh} to differences in the contact area between the surface and liquid according to the surface–liquid contact line. A schematically depicted liquid contact line between different liquids and the Pd/Ag dendrite surface is shown in Figure 6b. Both water and oil droplets on the superamphiphobic Pd/Ag dendrite surface were initially sitting on floating Pd/Ag leaves. In partial nanocavities of Pd/Ag leaves, as shown in Figure 6b (i), the water droplet tended to make less contact with the superamphiphobic surface than the oil droplet to minimize the total surface energy due to the high surface tension of the water droplet. On the other hand, oil or HD droplets, which have low surface tensions, made more contact with the superamphiphobic surface because the liquid–surface energy was lower than the air–surface energy [Figure 6b (ii)].³⁰ That is, the contact area between the oil and the superamphiphobic surface was larger than that between water and the surface under ambient air. Although adhesion of the oil droplet under ambient air was larger than that of the water droplet under ambient air, the sliding angles of both liquids were less than 10°, which indicates that both liquids maintained Cassie–Baxter states. Upon H_2 exposure, the expansion of Pd/Ag leaves had a greater effect on oil adhesion than on water adhesion, because the increase in contact area between the surface and the oil droplet was larger than that between the surface and the water droplet. Eventually, the increased contact area of the oil droplet resulted in a large ΔF_{adh} for the oil droplet, resulting in the droplet sticking firmly to the superamphiphobic surface; even the HD droplet was able to hang to the sticky superamphiphobic surface. Because our test liquids had high to low surface tensions in the order water, EG, oil, and HD, ΔF_{adh} showed the opposite order as shown in the graph in Figure 6c. When t_{Pd} was below 40 min, droplets rolled off the surfaces before and after H_2 exposure; these results showed that the ΔF_{adh} after volumetric expansion of the Pd layer was not able to hold the droplets on the surfaces. However, when the t_{Pd} was >100 min, the Pd/Ag dendrite surfaces lost their reversible switching adhesion ability because of wetting by oil and HD droplets. Deposition of a thicker Pd layer decreased the number of nanocavities in floating Pd/Ag dendrites because of agglomeration of Pd nanoparticles. Therefore, the air cavities between the liquid and surface reduced f , which decreased the CA and increased the pinning force between the liquid and surface. Sustainable reversible switching of liquid adhesion was observed without liquid residue or defects, indicating excellent control of adhesion of various liquids. This increase and decrease in HD droplet

adhesion was repeated for 10 cycles by changing the surrounding ambient atmosphere between air and 8% H_2 , as shown in Figure 6d. Droplet CAs remained >150° under different ambient conditions, indicating that the superamphiphobic state of the HD droplet on the Pd/Ag dendrite surface was stable. By using different adhesion forces for individual liquids under ambient H_2 , liquid selection for droplet-based microfluidics can be realized through Pd/Ag dendrite superamphiphobic surfaces with gas-induced switchable adhesion. Figure 5e and a Supporting Information video show picking and selecting of a liquid droplet on a Pd/Ag dendrite superamphiphobic surface. The surface could not capture both water and HD droplets under ambient air (Figure 5e, top pictures); however, the HD droplet was selectively picked by the superamphiphobic surface because of increased adhesion in response to 8% H_2 gas exposure (Figure 5e, bottom pictures). These differences in adhesion of different liquids to the Pd/Ag dendrite superamphiphobic surfaces could potentially be used to distinguish among liquids with various surface tensions in droplet-based microfluidics.

4. CONCLUSIONS

In summary, we reported a convenient method for obtaining superamphiphobic surfaces by synthesizing the Pd/Ag dendrites through electroless galvanic replacement reaction and post-perfluoroalkylthiol coating. The adhesive properties of the Pd/Ag dendrite superamphiphobic surfaces could be reversibly altered by exposure to different external atmospheres. The prepared surfaces had extremely low adhesion to various liquids under ambient air because of microscale overhang-like structures and leaf-textured Ag nanocavities. The adhesion of the oil-repellent surfaces to liquid droplets increased due to morphological changes in the Pd layer of the surfaces in response to external gaseous stimulation. The Pd layer expanded volumetrically under ambient H_2 because of diffusion of hydrogen atoms into the Pd lattice, which increased the contact area between droplets and surfaces, thereby increasing the adhesion force between them. Changing of the atmosphere allowed reversible adhesion switching of the superamphiphobic surfaces, because hydrogen atoms diffused out easily from the Pd atoms under ambient air. This is the first report of superamphiphobic surfaces with reversible adhesion switching abilities for which no elaborate efforts to recover the original state are required. We anticipate that by using our droplet-controlling system, novel applications for droplet-state samples can be implemented, regardless of the type of liquid.

■ ASSOCIATED CONTENT

Supporting Information

Additional SEM images, AFM images, optical images of liquid droplets, schematic depiction and derivation of adhesion force and change in adhesion force, and videos of sliding, pinning, and selecting of liquid droplets. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b01038.

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Notes

The authors declare no competing financial interest.

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