

Robust Superhydrophobic Carbon Nanotube Film with Lotus Leaf Mimetic Multiscale Hierarchical Structures

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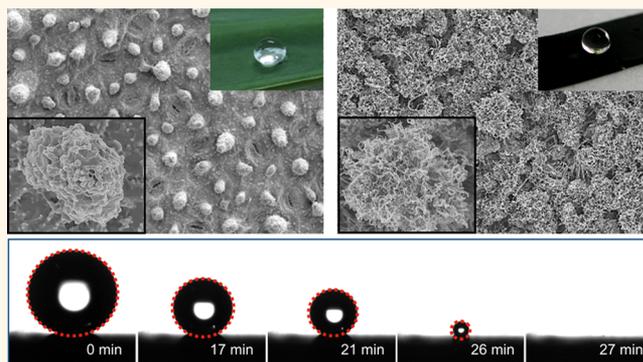
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S Supporting Information

ABSTRACT: Superhydrophobic carbon nanotube (CNT) films have demonstrated many fascinating performances in versatile applications, especially for those involving solid/liquid interfacial processes, because of their ability to affect the material/energy transfer at interfaces. Thus, developing superhydrophobic CNTs has attracted extensive research interests in the past decades, and it could be achieved either by surface coating of low-free energy materials or by constructing micro/nano-hierarchical structures via various complicated processes. So far, developing a simple approach to fabricate stable superhydrophobic CNTs remains a challenge because the capillary force induced coalescence frequently happens when interacting with liquid. Herein, drawing inspirations from the lotus leaf, we proposed a simple one-step chemical vapor deposition approach with programmable controlled gas flow to directly fabricate a CNT film with rather stable superhydrophobicity, which can effectively prevent even small water droplets from permeating into the film. The robust superhydrophobicity was attributable to typical lotus-leaf-like micro/nanoscale hierarchical surface structures of the CNT film, where many microscale clusters composed of entangled nanotubes randomly protrude out of the under-layer aligned nanotubes. Consequently, dual-scale air pockets were trapped within each microscale CNT cluster and between, which could largely reduce the liquid/solid interface, leading to a Cassie state. Moreover, the superhydrophobicity of the CNT film showed excellent durability after long time exposure to air and even to corrosive liquids with a wide range of pH values. We envision that the approach developed is advantageous for versatile physicochemical interfacial processes, such as drag reduction, electrochemical catalysis, anti-icing, and biosensors.

KEYWORDS: bio-inspired, superhydrophobic, carbon nanotubes, lotus leaf, hierarchical structures



Carbon nanotubes (CNTs) have emerged as one of the most amazing nanomaterials and have shown many excellent performances in various applications such as rechargeable batteries, drug carriers, catalyst supports, automotive parts, and sporting goods,^{1–3} due to their extraordinary physicochemical properties and good biocompatibility.⁴ In most cases, surface wettability of materials, especially those with extreme states (*i.e.*, superwettability), is a crucial parameter for various interfacial processes because it can influence or even determine the mass transfer and electron delivery behaviors at the interface.^{5–11} Therefore, CNT films with superwettability, including superhydrophobicity, superoleophobicity, and switchable superwettability, were developed extensively in the past decades and have shown excellent performances in versatile physicochemical interfacial processes such as self-cleaning, anti-icing, oil/water separation, drag reduction, electrocatalysis, biosensors, *etc.*^{12–25} Among them, the superhydrophobic CNT

film is particularly fascinating for its antiwater behavior, which can significantly affect the material/energy transfer for those solid/liquid interface associated applications. So far, research efforts on fabricating superhydrophobic CNTs were focused on two aspects: surface modification by inorganic/organic oxides or fluorides with low surface energy and constructing micro- and nano-hierarchical structures.^{26–30} However, these strategies suffer limitations of being time- and cost-consuming complicated preparation processes; meanwhile, the surface chemical modification can alter the CNTs' properties in many cases. Thus, developing a facile one-step approach to fabricate pure superhydrophobic CNT films remains a challenge.

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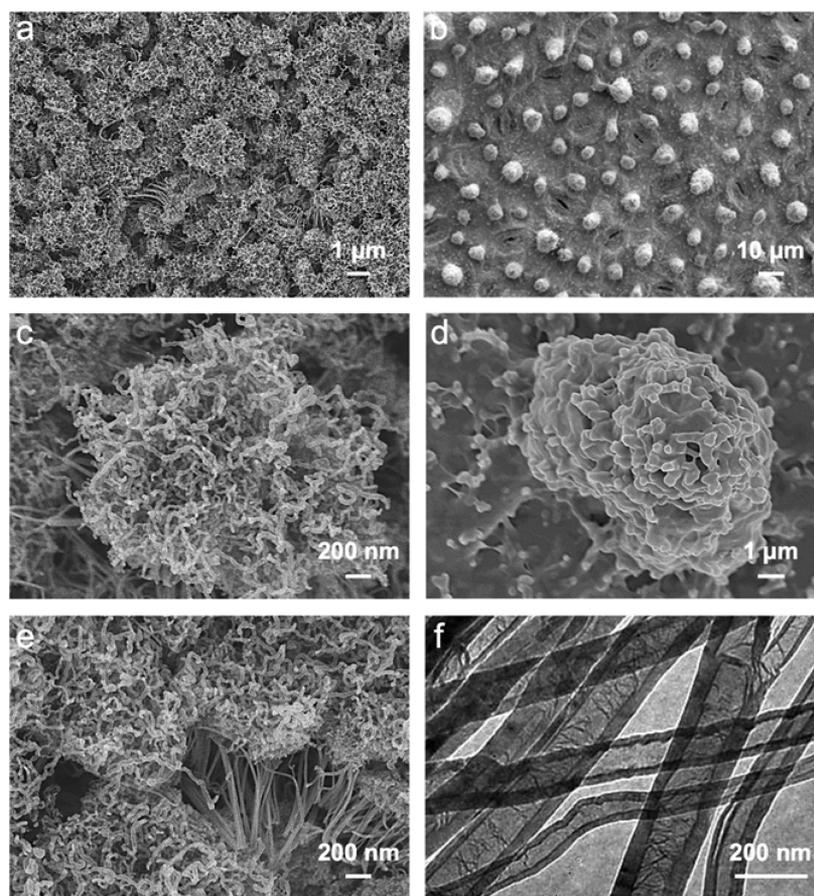


Figure 1. SEM images of (a) as-prepared lotus-leaf-like CNT film and (b) lotus leaf. High-magnification SEM images of the (c) microcluster on the as-prepared CNT film and (d) micropapilla of the lotus leaf. (e) Cross-sectional SEM image of the microcluster on CNT film, where the under-layer aligned CNTs can be seen clearly. (f) TEM image of the as-prepared CNTs.

In general, pure nanostructured CNT films can be wetted by water due to the capillary effect, despite their high water contact angles (CAs) at the very beginning of the water contact,^{31–35} which is attributable to the inherently lower hydrophobicity of the graphite outer-layer of CNTs (with a water CA of 84–86°)^{36–38} and the one-dimensional tubular structures. Driven by the capillary effect, water is liable to spread on such CNT films, and consequently, the alignment is collapsed and rearranged into microbundles. Preparing a superhydrophobic CNT film with stable water repellency is the most direct and efficient approach to escape such water imbuing effect, by which both the highly integrated topological structures and the physicochemical properties of CNTs can be maintained. Therefore, developing stable superhydrophobicity CNT films is still in demand.

Herein, drawing inspiration from the stable superhydrophobicity on the lotus leaf, we developed a one-step template-free chemical vapor deposition (CVD) method to prepare a lotus-leaf-like CNT film by controlling the manner of the gas flow, where the iron(II) phthalocyanine (FePc) was used as the carbon source and iron catalyst simultaneously. The as-prepared CNT film showed both static and dynamic superhydrophobicity, giving high water CAs greater than 150° even to water droplets with very small size and corrosive droplets with a wide range of pH, as well as the rather low water adhesion. We proposed that the robust superhydrophobicity was attributable to the micro/nanoscaled hierarchical surface topological nature of the as-prepared lotus leaf mimetic CNT

film, which enabled dual-scaled air pockets between the liquid/solid interface. Note that the inherent excellent physicochemical properties of CNTs was maintained for the as-prepared superhydrophobic CNT film as no further chemical modification was conducted. We envision that the stable superhydrophobic CNT film is advantageous for versatile physicochemical interfacial processes, such as electronic sensors,³⁹ air retention,⁴⁰ electrochemical reaction,⁴¹ and anti-icing.⁴²

RESULTS AND DISCUSSION

A lotus-leaf-like CNT film was prepared on a silicon wafer by the CVD method under programmable controlled gas flow of Ar/H₂ (1:2 v/v), which acted dually as carrier gas and reducing environment sustainer within the sealed tube. Typically, the gas flow was set at *ca.* 54 mL/min in the initial 2 min, then increased to *ca.* 108 mL/min for another 1 min, and finally slowed down again to *ca.* 54 mL/min for 2 min. By such strategy, the quasi-two-layer structured CNT film was prepared, exhibiting typical lotus-leaf-like surface topology. As shown in Figure 1a, many microsized CNT clusters with the diameter ranging from 1 to 2.5 μm were randomly distributed on the whole as-prepared CNT film, leaving many vacancies between. Each single microcluster was composed of numerous nanotubes, which entangled with each other and radially arranged toward the outside (Figure 1c), whereas the under-layer CNTs were mostly aligned with each other (Figure 1e). Thus, the as-prepared CNTs exhibited a typical hierarchical micro/nanostructure, showing topologic nature very similar to that

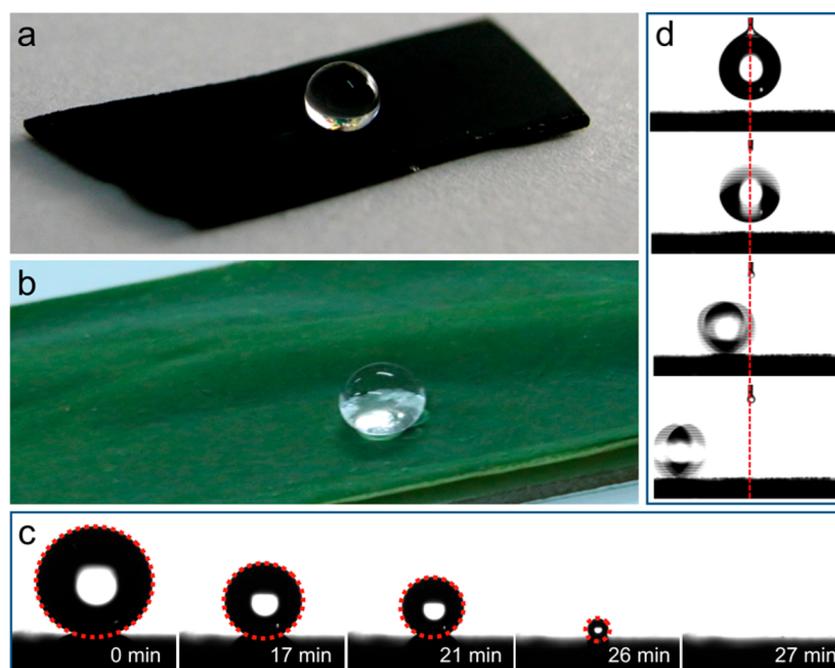


Figure 2. Photos of a large droplets ($\sim 5 \mu\text{L}$) placed on (a) as-prepared CNT film and (b) lotus leaf surface, suggesting the similar superhydrophobicity. (c) As-prepared CNT film shows outstanding repellency to even a tiny droplet: the droplet ($\sim 5 \mu\text{L}$) gradually shrank with time due to the evaporation when placed on the as-prepared CNT film, and in this process, the droplet maintained the perfect spherical shape with high water CA greater than 150° ($\sim 157.8^\circ$ in 0 min, $\sim 153.5^\circ$ in 17 min, $\sim 152.5^\circ$ in 21 min, and $\sim 150.2^\circ$ in 26 min) all the time. (d) Droplet ($\sim 5 \mu\text{L}$) quickly rolled off from CNT film with a tiny tilting angle ($1\text{--}3^\circ$).

of the lotus leaf. The representative surface structures of the lotus leaf are shown in Figure 1b,d, where numerous microscaled papillae were distributed randomly on the whole surface, with each papilla composed of a large number of nanoscaled branches. In addition, the inner-hollow tubular structure of the CNTs was characterized by transmission electron microscopy (TEM), where the diameter of CNTs was measured as *ca.* 100–150 nm (Figure 1f). The chemical carbon nature was confirmed by X-ray photoelectron spectroscopy (XPS) (Figure S1). As known, the combination of the micropapillae and the nanobranches was the key factor that allowed the lotus leaf to keep its superhydrophobicity in air.⁴³ Therefore, it is reasonable to expect that such lotus-leaf-like CNT film may present stable superhydrophobicity.

To investigate the wetting performance of the as-prepared CNT film, water CA and water adhesion property were characterized comprehensively. The as-prepared CNT film showed excellent water repellency. As shown in Figure 2a, when slightly placed onto the CNT surface, the water droplet ($\sim 5 \mu\text{L}$) stood as a perfect spherical shape, just like the droplet on a lotus leaf (Figure 2b). It clearly revealed the superhydrophobicity of the as-prepared CNT film. More importantly, when the water droplet gradually shrank due to the evaporation, the spherical shape of the water droplet could be maintained in the whole 27 min, and the water CA was kept greater than 150° (Figure 2c) even to a very small water droplet, suggesting a rather stable superhydrophobicity. There was no observable pinning of the triphase contact line (TCL) during the whole process, and the TCL changed with time, giving little chance for liquid to spread along both the wall of each single nanotube and the surface of CNT film. This means that the as-prepared CNT film can prevent even a very small sized water droplet from permeating into the film, which effectively avoids the capillary-induced liquid spreading into the

CNT film.^{44,45} Furthermore, the droplet ($\sim 5 \mu\text{L}$) could easily bounce up and roll off the as-prepared CNT surface effortlessly (Figure S2). Specifically, with a rather tiny tilting angle ($1\text{--}3^\circ$), the water droplet could quickly roll off from the CNT surface (Figure 2d). These results revealed that the water sliding angle (SA) of the CNT film was extremely low. Therefore, the as-prepared CNT film presented stable superhydrophobicity and very low water adhesion, just like the lotus leaf.

Generally speaking, there are four typical cases for antiwetting surfaces that can be defined as Wenzel state, Cassie state, “petal” state, and “gecko” state.⁴⁶ All of these states exhibit similar static high water CAs but different CA hysteresis due to the difference in surface topologic nature. Here, the large CA and the low hysteresis of the as-prepared CNT film, meaning typical Cassie state, are attributable to the typical lotus-leaf-like micro/nanoscaled hierarchical surface structures. As schematically shown in Figure 3a, the dual-scaled air pockets are formed within each microscaled CNT cluster and between, which enable the large decrease of the liquid/solid interface and thus lead to a stable superhydrophobicity. When a water droplet is set on the as-prepared CNT film, a large amount of air can be efficiently and stably trapped at the liquid–solid interface by two strategies: one is the air pockets within each single microcluster that is enabled by the numerous entangled nanotubes; the other is the air between microclusters. Such a composite interface endowed the CNT film a nano-Cassie state to repel even micrometer scaled water droplets. In comparison, the vertically aligned nanostructured CNT film was prepared by a similar CVD approach at a constant gas flow of Ar/H₂ (1:2 v/v, *ca.* 54 mL/min) for the entire growing process. The XPS spectra of the nanostructured CNT film showed a primary carbon element composition and a spot of Fe catalyst similar to that of the lotus-leaf-like CNT film (Figure S1). As shown in Figure 3b,c, CNTs were densely packed and almost normal to

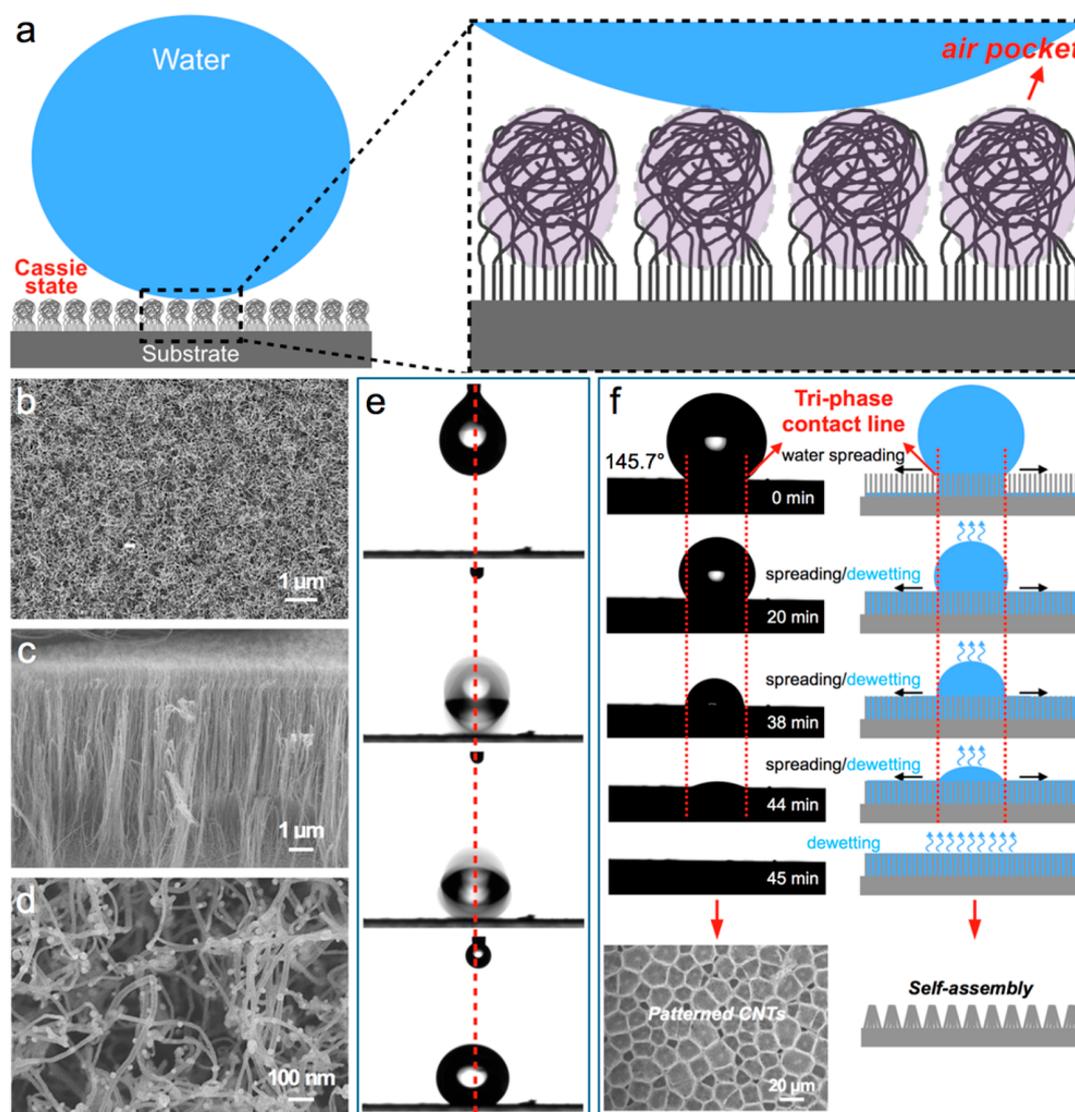


Figure 3. (a) Schematic diagram of the superhydrophobicity on the as-prepared lotus-leaf-like CNT film: micro/nanoscaled two-tier structures lead to a nano-Cassie contact. (b) Low-magnification SEM image of the nanostructured CNTs film. (c) Cross-sectional SEM image, showing CNT alignment. (d) High-magnification SEM image of the nanostructured CNT film. (e) Droplet ($\sim 5 \mu\text{L}$) directly stuck on the film without bouncing and rolling. (f) Dynamic process of the water droplet on the nanostructured CNT film, showing decreasing CA of $\sim 145.7^\circ$ in 0 min, $\sim 137.3^\circ$ in 20 min, $\sim 90.1^\circ$ in 38 min, and $\sim 31.5^\circ$ in 44 min, and as a result, the film became a hydrophilic one, during which process the patterned CNTs formed by water spreading.

the substrate, whereas the top of the nanotubes entangled with each other (Figure 3d). Distinct from the lotus-leaf-like CNT film, when putting a droplet ($\sim 5 \mu\text{L}$) onto the vertically aligned nanostructured CNT film, the droplet directly stuck on the film without bouncing and rolling (Figure 3e). Further testing demonstrated that the water SA of the nanostructured CNT film was as large as $\sim 62.3^\circ$, indicating very large adhesion to water. Although the densely packed nanostructured CNT film showed a large water CA of *ca.* 145.7° that arised from the air temporarily trapped at the liquid/solid interface at the beginning (Figure 3f), the CA gradually decreased over time, and then the film turned into an apparent hydrophilic state. In this process, illustrated by a red dotted line, the liquid/solid/gas TCL was pinned and kept steady all the time on the top surface of the CNT film, providing a large liquid/solid interacting interface. As shown in the schematic diagrams (Figure 3f, right), with prolonged time, water could be guided into the spaces between the aligned nanotubes under the capillary force, as has been

reported previously.^{31,32} Then, water gradually spread to the substrate due to the hydrophilicity of the silicon substrate, and the CA became smaller accordingly. Finally, as we previously reported, after the water evaporated, micropatterns were formed on the CNTs as a consequence of bending and bundling/self-assembly of the vertically aligned CNTs. These results further confirmed that the hierarchical micro/nanoscaled two-tier structure played a crucial role in the stable superhydrophobicity of the as-prepared lotus-leaf-like CNT film.

To explore the stability of the superhydrophobicity on the as-prepared lotus-leaf-like CNT film, the effects of both the exposure time to air and the liquids with different pH values were examined. As shown in Figure 4a, when exposed to air with $\sim 60\%$ humidity, the as-prepared lotus-leaf-like CNT film gave high water CAs greater than 150° during the whole process without any observable decrease. After 8 weeks of exposure, the water CA gave a value of *ca.* 152.7° , indicating a long-term durable superhydrophobicity. Furthermore, the as-

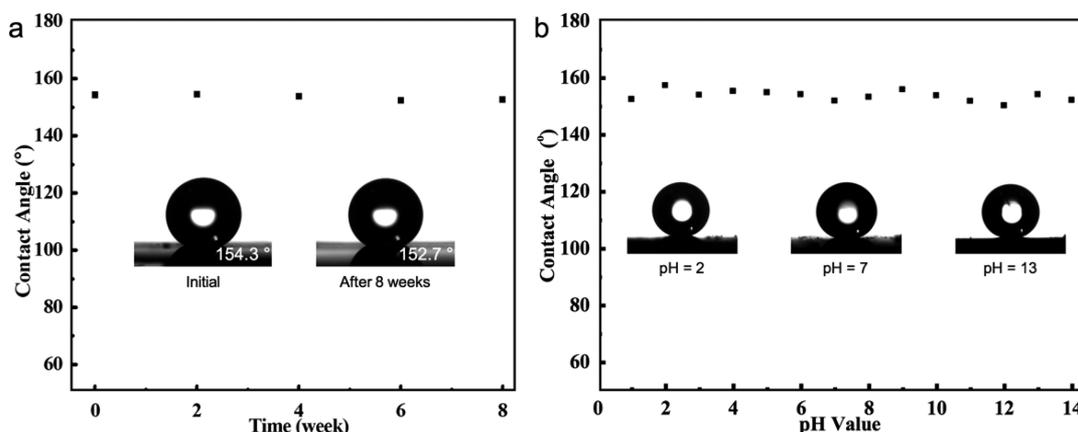


Figure 4. (a) Water contact angles of the lotus-leaf-like CNT film after long exposure time to air with $\sim 60\%$ humidity, showing rather high water CAs during the whole process ($\sim 154.3^\circ$ at 0 weeks, $\sim 154.9^\circ$ at 2 weeks, $\sim 153.3^\circ$ at 4 weeks, $\sim 151.8^\circ$ at 6 weeks, and $\sim 152.7^\circ$ at 8 weeks). (b) CAs of corrosive liquids with different pH values from 1 to 14 ($\sim 152.8^\circ$ in pH 1, $\sim 158.0^\circ$ in pH 2, $\sim 154.5^\circ$ in pH 3, $\sim 155.7^\circ$ in pH 4, $\sim 155.2^\circ$ in pH 5, $\sim 154.7^\circ$ in pH 6, $\sim 152.2^\circ$ in pH 7, $\sim 153.4^\circ$ in pH 8, $\sim 156.3^\circ$ in pH 9, $\sim 154.2^\circ$ in pH 10, $\sim 152.4^\circ$ in pH 11, $\sim 152.0^\circ$ in pH 12, $\sim 154.6^\circ$ in pH 13, and $\sim 152.3^\circ$ in pH 14) on the as-prepared lotus-leaf-like CNT film, demonstrating excellent repellency to corrosive liquids.

prepared lotus-leaf-like CNT film also exhibited excellent repellency to corrosive liquids. As shown in Figure 4b, droplets of corrosive liquids with different pH values were carefully placed onto the lotus-leaf-like CNT surface to evaluate their CAs. Changing the droplets from strong acid (pH 1) to strong base (pH 14), the measured CAs were all above 150° . Such excellent repellency to corrosive liquids was attributable to the synergistic effect of highly chemical stability of CNTs and the hierarchical rough structures of the lotus-leaf-like surface. As numerous air was trapped within the micro/nanoscaled structure, the formed dual-scaled air pockets prevented the infiltration of water droplets and corrosive species. Taken together, the as-prepared lotus-leaf-like CNT film with multiscale hierarchical structures enable a stable and robust superhydrophobicity, which is an advantage for limiting the interaction with corrosives species. Here, the robust anti-corrosive superhydrophobic property endows the CNT film potential applications in various industries and daily life.

CONCLUSIONS

In summary, a simple one-step template-free CVD method to fabricate a lotus-leaf-like stable superhydrophobic CNT film was developed. Attributed to the typical micro/nanoscaled hierarchical structure, the as-prepared CNT film showed stable static and dynamic superhydrophobicity even with very small sized droplets. The air was trapped by the CNT surface, forming dual-scaled air pockets, which largely reduced the liquid/solid contact and endowed a stable Cassie state water contact on the CNT surface. Moreover, the superhydrophobicity of the CNT film is rather stable, even being exposed to air with certain humidity. Also, the CNT film exhibited excellent repellency to corrosive liquids with a wide range of pH values, indicating good chemical etching resistance. Combining the stable superhydrophobicity and the excellent inherent physicochemical properties of CNTs, the as-prepared lotus-leaf-like CNT film is advantageous for various practical interfacial applications, such as superhydrophobic electrodes in gas-consuming electrochemical reactions, antifogging/icing electromagnetic wave-absorbing materials, and biosensors. After functionalization by emerging surface modification

methods, this stable superhydrophobic CNT film will provide a platform for various applications.^{47,48}

EXPERIMENTAL METHODS

Substrate Fabrication. Carbon nanotube films were prepared on cleaned silicon wafers by pyrolysis of iron(II) phthalocyanine (FePc) containing both the carbon source and the metal catalyst required. FePc (0.23 g) in a quartz boat was decomposed at approximately 550°C , and the carbon nanotube films were prepared at approximately 900°C in a flow reactor consisting of a quartz tube and a tube furnace fitted with a temperature controller under Ar/H₂. For lotus-leaf-like CNT film, the gas flow was set at *ca.* 54 mL/min at the initial 2 min, increased to *ca.* 108 mL/min for 1 min, and finally slowed down again to *ca.* 54 mL/min for 2 min. For nanostructured CNT films, the gas flow was set at *ca.* 54 mL/min for the entire 5 min growth.

Surface Characterization. SEM images were obtained on a JEOL JSM-6700F scanning electron microscope at 3.0 kV. The TEM image was obtained with a Hitachi JEM 200-CX instrument at 120 kV. The CAs and SAs were measured using a contact angle system (OCA 20, Dataphysics, Germany) at ambient temperature with the probe liquids. Here, for each sample, five testing positions were selected randomly, and the averaged value was given. XPS data were obtained with electron spectrometer (ESCALab220i-XL, VG Scientific, United Kingdom). The dynamic wetting processes of the lotus-leaf-like and nanostructured CNT films were recorded with a high-speed camera.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b06371.

XPS spectra of the carbon nanotube films and images of a droplet ($\sim 5\ \mu\text{L}$) that easily bounced up and rolled off when released onto the lotus-leaf-like carbon nanotube film (PDF)

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Notes

The authors declare no competing financial interest.

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