A short-range ordered–disordered transition of a NiOOH/Ni(OH)₂ pair induces switchable wettability†

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By virtue of its amorphous structure with a short-range order feature, the inorganic nanoporous nickel oxyhydroxide (NiOOH) can reversibly and rapidly switch wettability by alternate treatments of environmental chamber (superhydrophobic) and UV/ozone (superhydrophilic). The switchable mechanism of the NiOOH/Ni(OH)₂ pair arising from its exceptional intrinsic short-range order–disorder transition together with chemical composition change is highlighted for the first time, which significantly differs from the current stimuli-responsive materials. This distinct multifunctional thin film not only possesses reversible wettability but also is optically patternable/repairable and electrically conductive, which could be applicable in the manufacturing of various micro- and nanostructures. We demonstrate this potential in the rewritable two-dimensional (2D) microfluidic channels and wetting-contrast enhanced selective electroplating.

Introduction

The ability of plants to adapt to various habitats includes a range of unique wetting properties such as low-adhesivity/superhydrophobicity in the lotus leaf and high-adhesivity/superhydrophobicity in the peanut leaf.1 Human-engineered analogues of superhydrophobic surfaces are commonly synthesized from hierarchies permanently modified with low surface energy materials so that they allow only one-way wetting transitions.2 Recently, stimuli-responsive materials which are dynamically adaptive to the external environment, with reversibly switchable and rewritable wettability, have become attractive for various applications, including micro-patterning, cell encapsulation, microfluidic channels, and drug delivery.3,4 A variety of organic and inorganic materials based on the responsive mechanisms of single stimulus or multi-stimuli have been developed.3,5,6 However, the sharp trade-off between the response time and the wettability switching range limits their widespread use. Most organic materials, such as photosensitive azobenzene, thermal-responsive poly(N-isopropylacrylamide) (PNIAAm), and solvent-responsive block copolymers consisting of polystyrene and poly(acrylic acid), offer rapid responses (of several minutes) to versatile stimuli but show small changes (<40°) in their water contact angles (WCAs) due to their inherently smooth surfaces.7–10 To widen the switching range, additional fabrication processes or polymer nanocomposites are usually implanted to roughen the surface, which increases the process complexity. In contrast, inorganic materials have intrinsically superior switching ranges (>70°) and readily form the micro-/nano-/hierarchical structures required to reach a widely switchable wettability.11–13 For example, two photosensitive inorganic materials, aligned nanorod ZnO films and lotus leaf-like TiO₂, enable the switching range between superhydrophobic and superhydrophilic.14–16 Compared to organic materials, inorganic materials usually have lower toxicity and greater photochemical/thermal stability. Nevertheless, the relative long response time (several days or weeks) upon dark storage poses a significant hurdle for their practical application.12 It is thus imperative to develop a new stimuli-responsive material that has both rapidly responsive synergic features and wide switching ranges between superhydrophilic and superhydrophobic. More importantly, if such a stimuli-responsive material could be easily patterned with readily available trigger sources, it would be viable for use in industry.

As an earth-abundant semiconductor, nickel oxyhydroxide/nickel hydroxide (NiOOH/Ni(OH)₂) is used in a diverse range of highly technological applications.17–19 Nearly all of its applications are focused on its optical, electrochromic, and electrochemical properties. In a previous study, we demonstrated its great promise in terms of tunable wettability, changing
from superhydrophilic to superhydrophobic via the chemical modification of low surface-energy ODS-SAMs. However, the irreversible one-way nature of the wetting transition limits its flexibility too much for use in many cutting-edge applications. In this paper, we further explore the switchable wettability of amorphous and nanoporous (AN) NiOOH/Ni(OH)$_2$. Aria and Gharib applied ultraviolet (UV)/ozone and vacuum pyrolysis treatments to the carbon nanotubes to reversibly tune the wettability between hydrophilic and superhydrophobic due to the oxygen adsorption and desorption. Similarly, without the need for surface chemical modification, alternately exposing the AN NiOOH/Ni(OH)$_2$ to an environmental chamber (EC, at 85 °C, 70% relative humidity and normal pressure) and UV/ozone enables a rapid, reversible and widely switchable wettability between (super)hydrophobic and superhydrophilic. Interestingly, the mechanism is based on its exceptional intrinsic short-range order–disorder transition together with chemical composition change, which is highlighted for the first time. Furthermore, we found that this electrically conductive film is easily patternable and repairable, both of which are essential properties for use in smart microelectronic devices. The effectiveness of these functions was demonstrated through rewritable two-dimensional (2D) microfluidic channels and wetting-contrast enhanced selective electroplating.

**Experimental section**

**Fabrication of wettability-switchable film**

The experiments were carried out using an anodically electroplated NiOOH/Ni(OH)$_2$ film on flat FTO glass ($R_{\text{rms}}$: 30.4 nm) and rough SS ($R_{\text{rms}}$: 110.4 nm). The electrolyte was composed of 0.39 M nickel sulfate, 0.1 M sodium sulfate, and 0.13 M sodium acetate, which was the carbonyl source indicated in the XPS. An electrochemical workstation (CHI 660E) was applied to a standard three-electrode system with the clean FTO or SS as the working electrode, a platinum mesh as the counter electrode, and a saturated Ag/AgCl as the reference electrode. A three-step constant current density deposition was used, starting from a current density of 0.005 mA cm$^{-2}$, then increasing to 0.05 mA cm$^{-2}$ and continually increasing to 0.5 mA cm$^{-2}$ for every 30 min at room temperature (see Fig S1, ESI†). The reasons for using three-step anodic electrodeposition are explained in our previous work. The deposited film exhibited the same electrical conductivity (7.6 Ω cm$^{-1}$) as the bare substrates even after exposure to EC at 50 °C and 85 °C with 70% RH (HongHui, THH80L) or a hot plate at 100 °C for 60 min and UV/ozone (Kingo, TK-110) for 10 min.

**Optical patterning process**

As shown in Fig. 1(a), a UV/ozone-resist sticker was ablated with a CO$_2$ laser (Universal Laser System) to arbitrarily generate the desired mask on the microscale, including the Y-shaped and the ‘smiling face’ pattern for the rewritable 2D microfluidic channels, and the vertical strips for the wetting-contrast enhanced selective plating. Secondly, the patterned mask was attached to the Ni(OH)$_2$-coated FTO surface (WCAs ~ 139°) and then exposed to UV/ozone (WCAs of exposed area <4°). Lastly, after the sticker was removed, a superhydrophilic–hydrophobic pattern was produced in two applications. Before rewriting a new pattern, ethanol was used to remove the sticker residue. Fig. 1(e) is a schematic of Y-shaped microfluidic channels. Commercial gold (Samtec) and nickel (Caswell) electrolytes were used for electroplating for 270 s.

**Characterization**

WCAs were measured using a contact angle goniometer (Sindatek Model 100SB) at five points. The film’s atomic structure, morphology, crystallinity, and chemical state were determined by HRTEM (Tecnai, G220S-Twin), FE-SEM (Hitachi S-4800), grazing-angle XRD (Rigaku Smartlab) with an incident angle of 0.15°, and XPS (Physical Electronics 5600).

**Results and discussion**

AN NiOOH with a thickness of 600 nm was deposited on flat fluorine-doped tin oxide (FTO) glass (see Fig. 2(a) and (b)) and the rough stainless steel (SS) via stepwise anodic electrodeposition, which is cost-effective and relatively fast, and in which it is easy to control and reproduce surface morphologies. Fig. 2(c) shows the reversible wettability of the AN NiOOH/Ni(OH)$_2$-coated substrates. The as-prepared nanoporous film on FTO was dark and superhydrophilic (6.9 ± 1°). After heating on a hot plate (100 °C), the film became transparent and hydrophobic (112.5 ± 5°). This change in coloration implied a change in the chemical composition within the film. The EC (85 °C, 70% RH) was introduced to the heat treatment with sufficient water vapor. The WCAs increased to 138.9 ± 3° after exposure to the EC, indicating that water vapor plays an important role in mediating wettability. When the surface was irra-
diated with UV/ozone (265 nm), the color and WCAs were restored to their initial states. The film not only possesses long-term stability stored under an ambient atmosphere but also has good reversibility for more than 10 cycles (Fig. S2†).

Using the rough SS (Fig. S3†) instead of the flat FTO as a substrate further broadened the switchable wettability ranging from superhydrophilic (4.1 ± 1°) to superhydrophobic (153.2 ± 2°) due to the improved 3D capillary effect and the air-trapping effect.24,25 An excellent water-repellency (see video S2†) on a NiOOH/Ni(OH)2-coated SS was achieved. The adhesion force between the water droplet and the sample was calculated to be around 33 μN (see Fig. S4†).26

Conventional X-ray diffraction (XRD), as shown in Fig. S5† revealed amorphous features in the films coated on FTO under different treatment conditions. Further atomic-scale information was acquired from high-resolution transmission electron microscopy (HRTEM).

As shown in Fig. 3(a), the as-prepared film was short-range ordered γ-NiOOH with a basal spacing of 6.7 Å, in which the atomic packing of layered nanosheets was in the [00l] direction with intercalated water molecules and alkali metal ions.27 The intersheet distance was found to be slightly shorter than the theoretical value (6.9 Å), which may be attributed to the lattice distortion.28 Because the sponge-like nanoporous structure can enhance the 3D capillary effect and the edge plane of γ-NiOOH has a high affinity toward water, the combined effect results in superhydrophilicity.24 When subject to the EC of 50 °C and 70% RH (called low EC, hereafter), trivalent γ-NiOOH was reduced to short-range ordered α-Ni(OH)2 with an expanded basal spacing of 7.6 Å, and the WCAs increased to near 90° due to the hydrophobic basal plane of Ni(OH)2, as shown in Fig. 3(b).29 According to eqn. (1), the chemical reaction induces the composition change from NiOOH to Ni(OH)2 when consistently supplied with water vapor.23

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\text{NiOOH} + \text{H}_2\text{O} + e^- \rightarrow \text{Ni(OH)}_2 + \text{OH}^- \tag{1}
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The α-Ni(OH)2 belongs to simple layered double hydroxide (Ni-LDH), which is constructed from a stacked Ni(OH)2−x layer (symmetry: D_{3h} or O_{h}) intercalated with anions and water molecules (C_{2v}) in between. As noted, the unmatched symmetry between water molecules and Ni(OH)2−x layers inevitably causes defects due to turbostratic disorder (α-Ni(OH)2) but maintains a short-range order along the [00l] direction.30

As shown in Fig. 3(c), heating at relatively high temperatures of 85 °C and 70% RH (called high EC, hereafter) caused not only the chemical composition to change but also caused an order–disorder transition of Ni(OH)2, where the edge plane was ill-defined and the layered structure had completely disappeared. This could be explained by the local rearrangement of crystallographic orientation to optimize the hydrogen bonding between the thermal-diffused/intercalated water and the Ni(OH)2−x layer.31,32 From a thermodynamic point of view, the short-range ordered Ni(OH)2 layers tilt by a certain angle to enable their lowest surface-energy (00l) planes to face towards air (see Fig. S6†), leading to a nanoscale discontinuous three-phase contact line (TCL).1 As a result, the presence of disordered structures tends towards air traps rather than water adsorption to further increase WCAs. Fig. 4 illustrates the mechanism of de-wetting evolution from as-prepared to high EC treated samples, where the hydrophobic regions are extended from the basal plane (low EC) to the edge plane

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**Fig. 2** FE-SEM images of the as-prepared film from (a) top and (b) side view. (c) Reversible change in the wettability of the as-prepared film and its alternate exposure to different heat sources and UV/ozone on FTO and SS.

**Fig. 3** HR-TEM images of (a) as-prepared film and its exposure to (b) low EC, (c) high EC for 1 h, and (d) UV/ozone for 10 min.
(high EC) of Ni(OH)₂ after the EC treatment. Taking advantage of the mild oxidation and hydrolyzation caused by UV/ozone to provide hydroxyl radicals, the film returned to a superhydrophilic γ-NiOOH phase, as shown in Fig. 3(d).33

To mitigate undesired substrate signals, grazing incidence XRD was used to evaluate the global film evolution arising from the chemical composition change and the short-range order–disorder transition as shown in Fig. 5.34 The peak positions of the amorphous hump were located at 13.2° for as-prepared and UV/ozone samples, corresponding to the prominent basal reflection (001) of crystallized γ-NiOOH, and the peak at 11.6° for the low EC treated sample corresponding to α-Ni(OH)₂. The relatively low intensity of the high EC treated film provides evidence for the disordered characteristics outlined previously.35

X-ray photoelectron spectroscopy (XPS) provided not only the surface chemical state but also the surface water adsorption, enabling us to construct a comprehensive picture of the film’s surface status, as shown in Fig. 6. In the Ni 2p region, as-prepared and UV/ozone treated samples exhibit identical spectra with two peaks centered at 856.6 eV and 873.9 eV, corresponding to Ni 2p₃/₂ and Ni 2p₁/₂ for γ-NiOOH, respectively. The high EC treated sample, however, shifts to the lower binding energy at 855.2 eV and 872.9 eV corresponding to Ni 2p₃/₂ and Ni 2p₁/₂ for Ni(OH)₂, respectively.36 O 1s spectra of as-prepared and UV/ozone-treated samples were deconvoluted into four peaks assigned respectively to lattice O²⁻ (529.5 eV), OH⁻ (531.1 eV), carbonyl groups (531.7 eV) and hydroscopic H₂O (532.2 eV), whereas the high EC treated sample was only composed of OH⁻ (531.1 eV) and carbonyl groups (531.7 eV).37 Table S1† shows that the normalized O²⁻/OH⁻ ratios for the as-prepared, high EC treated and UV/ozone-treated samples were 0.97, 0 and 0.32, respectively, indicating that the as-prepared stoichiometric γ-NiOOH was converted to surface water-deficient Ni(OH)₂ via EC treatment, and then transformed into OH⁻-enriched γ-NiOOH after UV/ozone irradiation. The amounts of hydroscopic H₂O can be taken as a good index of surface affinity towards water, which is in good agreement with the wetting behavior of the as-prepared and UV/ozone treated samples and the de-wetting behavior of the EC treated sample. As noted, the relatively strong hydroscopic water peak of the UV/ozone treated sample is believed to result from the high amount of hydroxyl radicals generated during the UV/ozone process. The resulting OH⁻-enriched γ-NiOOH can enhance water adsorption, leading to low WCAs.

To advance our understanding of the kinetic mechanism, the time dependence of WCAs upon EC treatment at 85 °C and 120 °C was monitored, as shown in Fig. 7.

The experimental data were fitted to the dynamic Cassie model. We assume that the composite film surface purely con-
where \( \theta \) is the Avrami exponent. Two theoretical boundary conditions at \( t = 0 \) and \( t = \infty \) represent the pure ordered NiOOH and the pure disordered Ni(OH)\(_2\) constitutions, respectively. The fitting exponent \( n \) is 1.55, which belongs to 2D nucleation/growth. The initial ordered NiOOH coverage is 100% \((a = 1)\), which is consistent with the XPS results. According to \( k \) values of a rate constant at two different temperatures, the Arrhenius activation energy is 18.48 kJ K\(^{-1}\). This value is on the same scale as the reported activation energy for electrical reduction from NiOOH to Ni(OH)\(_2\).\(^{35}\) Here we summarize a model that explains this dewetting evolution, including sequential reactions induced by thermal energy and water vapor: (i) short range ordered \( \gamma \)-NiOOH converts to short-range ordered \( \alpha \)-Ni(OH)\(_2\) and (ii) defect-driven crystallographic rearrangement between thermal-diffused/intercalated water and the Ni(OH)\(_{2-x}\) layer to form disordered Ni(OH)\(_2\).\(^{35}\)

As mentioned above, AN NiOOH/Ni(OH)\(_2\) film has achieved a rapid response for switchable wettability between superhydrophilic and [super]hydrophobic without changing its surface morphologies. These outperforming features could be used in a wide variety of applications. We demonstrate here two such potential uses: rewritable two-dimensional (2D) microfluidic channels and wetting-contrast enhanced selective electroplating on FTO substrates. The representative patterning process is depicted in Fig. 1. Fig. 8(a)–(g) and video S3,\(^\dagger\) a real-time recording, show the microfluidic flow along the superhydrophilic paths with a width of 264 \( \mu \) m observed with optical microscopy. The microfluidic drops propagated along the superhydrophilic NiOOH domain and distributed into the branches, propelled by surface-tension confinement and capillary force.\(^{40}\) In previous studies, the reported 2D microfluidic channels, which were usually patterned by photolithography or inject/stamp printing, formed a virtual wall between the hydrophobic and hydrophilic domains to restrict the overflow from the channel but differed in their physical microthickness.\(^{41}\) Compared to these methods, our cost-effective patterning approach creates the “real” 2D bounded flow without a height difference to remarkably reduce the air friction, resulting in a flow speed of 0.82 mm s\(^{-1}\) using deionized (DI) water as microdrops. The high reversibility allows us to erase the Y-shaped pattern using high EC treatment and then rewrite a smiling face following the same patterning process, as shown in Fig. 8(h). Fig. S7\(^\dagger\) displays the wet eyes and mouth on the dry face, demonstrating how easily an arbitrary pattern with high wetting contrast can be reproduced.

Direct selective metal plating is of great interest for smart microelectronic devices due to material saving and fabrication simplification. The deposition principle is to control the native differences of the substrate activities, such as doping polarity, seed cultivation, or functionalized tailored groups.\(^{42,44}\) We discovered that the extreme wetting contrast is capable of opening a voltage window for selective electroplating. As shown in Fig. 9(a), gold electrodeposited on the superhydrophilic NiOOH-coated FTO surface requires a less negative onset potential \((-0.94 \, V)\) than that on the hydrophobic Ni(OH)\(_2\)-coated FTO \((-1.14 \, V)\). A similar trend can be observed in electroplated nickel, as shown in Fig. S8(a).\(^\dagger\) The strip pattern was defined using the process shown in Fig. 1 and gold was then electroplated at a voltage of \(-1.0 \, V\) within the operation window. Fig. 9(b) shows that only the predetermined superhydrophilic NiOOH strips were selectively electroplated. The
selectively electroplated nickel can be reproduced using the same process (see the inset of Fig. S8(a)). This wetting-contrast enhanced selective electroplating occurs when operating within the optimum voltage range because the superhydrophilic NiOOH surface has a high surface energy, leading gold to preferentially deposit on it to reduce the total surface energy. The hydrophobic Ni(OH)₂ surface has a low surface energy that blocks gold deposition. Fig. S8(b) shows that gold nanoparticles only nucleate and grow on the scaffolds of the hydrophobic Ni(OH)₂ film even at high overpotential (−2 V), demonstrating the great lyophobicity of gold electrolytes.

Conclusions

In summary, we have presented a wettability switchable material of the AN NiOOH/Ni(OH)₂ film that demonstrates a synergy between the response time and switching ranges. A switching cycle starting from superhydrophilic to superhydrophobic (in an EC of 85 °C, 70% RH) and reversing back to superhydrophilic (in an EC of 85 °C, 70% RH) are expected to open up a new approach in a wide variety of applications. Here, two such potential applications, rewritable 2D microfluidic channels and the wetting-contrast enhanced selective electroplating, have been demonstrated via a cost-effective optical patterning technique.

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Notes and references