

Electronic Supplementary Information (ESI)

Electrochemical Fabrication of Transparent Nickel Hydroxide Nanostructures with Tunable Superhydrophobicity/Superhydrophilicity for 2D Microchannels Application

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Fig. S1 shows the FE-SEM images of the bare-FTO and the anodic electroplating of Ni(OH)₂ films under 0.5 mA/cm² and 0.005 mA/cm² for 90 minutes, respectively. Compared with **Fig. 2**, the pore size distribution of **Fig. S1(a)** (0.5 mA/cm² for 90 minutes) is similar to **Fig. 2(d)** (0.5 mA/cm² for 30 minutes) and **Fig. S1(b)** (0.005 mA/cm² for 90 minutes) is similar to **Fig. 2(f)** (0.005 mA/cm², 0.05 mA/cm² and 0.5 mA/cm² for 90 minutes), indicating that pore size is dominated by the initial current density. In addition, the high contrast in SEM image of **Fig. 2(f)** proves that stepwise increase of current density is time-saving to impart appropriate roughness.

As mentioned before, roughness plays an important role in adjusting the wettability. **Fig. S2** shows the AFM images of bare-FTO and Ni(OH)₂/FTO. Obviously, roughness is increased with increasing deposition steps, leading to increase the hydrophilicity.

The earth-abundant nickel hydroxide was chosen due to its inherent hydrophilic property of hydroxyl groups which could be switched into (super)hydrophobic property by interacting with alkoxy groups of self-assembled monolayers (SAMs) with long hydrocarbon

chains. Muthurasu and Ganesh reported that the surface coverage of SAMs on a substrate could be quantitatively calculated from AC impedance spectra, as shown in equation S2. (A. Muthurasu, V. Ganesh, *Journal of Colloid and Interface Science* **2012**, 374, 241)

$$\theta_{imp} = 1 - \frac{R_{ct,o}}{R_{ct}} \quad (S1)$$

where θ_{imp} is the surface coverage of SAMs, $R_{ct,o}$ is the charge transfer resistance of a bare substrate and R_{ct} is the charge transfer resistance of a SAMs modified substrate, which could be derived from fitting a standard Randle's equivalent circuit model. Here the 2 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple was used as a probing electrolyte. As shown in **Fig. S3**, the $R_{ct,o}$ of bare-FTO is $173\Omega\text{cm}^2$, the R_{ct} of ODS/FTO is $7,059\Omega\text{cm}^2$ and ODS/1-Ni(OH)₂/FTO is $46,993\Omega\text{cm}^2$, reflecting that the surface coverage of ODS monolayers was significantly enhanced from 97.55% to 99.63% by introduction the nanoporous Ni(OH)₂ film. Of course, not only the existence of hydroxyl groups but also the increased effective area of rough Ni(OH)₂ film contribute to the compact coverage of ODS monolayers.

In principle, the hydrophobicity on rough surface has been theoretically described by two basic models, one is the Wenzel's model and the other is the Cassie-Baxter's model. In the Wenzel's model, the liquid droplet is assumed to completely penetrate into the asperities of the rough surface as described, relating the roughness to the apparent water contact angles (WCAs), as shown in equation S1.

$$\cos\theta_w = R_{f,w} \cos\theta_0 \quad (S2)$$

where $R_{f,w}$ is the roughness factor which is equal to the ratio of actual surface area to the apparent surface area and θ_0 is WCAs of a flat surface while the θ_w is the WCAs of a rough surface. Considering the WCAs of bare-FTO is the θ_0 and the WCAs of nickel hydroxide

film coated FTO glass is θ_w , then the roughness factor of nanoporous nickel hydroxide film could be simply derived from equation S2. Taking the WCAs of $109.4 \pm 5.6^\circ$ on ODS/FTO as θ_0 , the theoretically WCAs of ODS/Ni(OH)₂/FTO based on the Wenzel's model could be simply calculated, as shown in Fig. S5. As seen, the theoretical values are quite deviated from the experimental results. It was worthy to note that the morphology and roughness of ODS/3-Ni(OH)₂/FTO was mainly determined by the underneath nanostructured nickel hydroxide film rather than the surface ODS monolayers, as shown in Fig. S4. As a result, only taking roughness increase after depositing nickel hydroxide film on FTO (from 30.4nm to 41.4nm) into consideration was unable to well explain the hydrophobicity increase.

On the other hand, Cassie-Baxter's model assumes that the water droplet is suspended on the top of the surface asperities and the air pockets, predicting that the hydrophobicity increases with increasing the surface roughness and the fraction of the air pockets. The apparent WCAs in this case is given by equation S3.

$$\cos\theta_A = R_{f,CB}f_{sl}\cos\theta - f_{lv} \quad (\text{S3})$$

where f_{sl} is the area fraction of solid-liquid interface, f_{lv} is the area fraction of liquid-air interface and $R_{f,CB}$ is the roughness factor of Cassie-Baxter's model. In addition, the sum of f_{sl} and f_{lv} is equal to 1. Assuming that the $R_{f,CB}$ is equal to the abovementioned $R_{f,w}$ and the area fraction of liquid-air (f_{lv}) is the ratio of the porous area to the total area, which could be derived from the FE-SEM images in Fig. 1 by imaging software (imageJ), as shown in the insets in Fig. S5. The corresponding f_{lv} for ODS/1-Ni(OH)₂, ODS/2-Ni(OH)₂ and ODS/3-Ni(OH)₂ are 0.41, 0.64 and 0.75 respectively. **Fig. S5** shows that our experimental results are in good agreement with Cassie-Baxter's models.

Fig. S6 shows the sliding angle of ODS/3-Ni(OH)₂ is around 5°

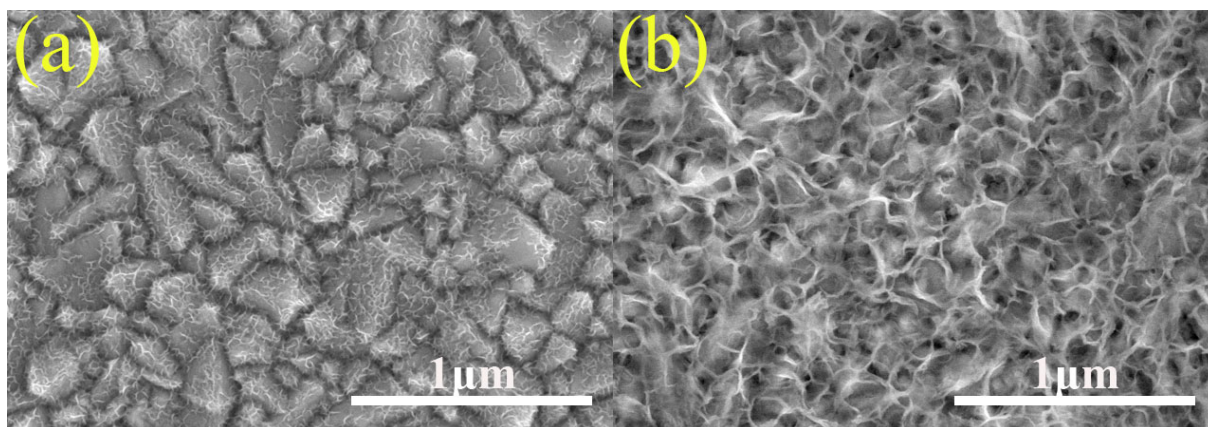


Fig. S1. FE-SEM images of Ni(OH)₂ films under (a) 0.5 mA/cm² and (b) 0.005 mA/cm² for 90 minutes.

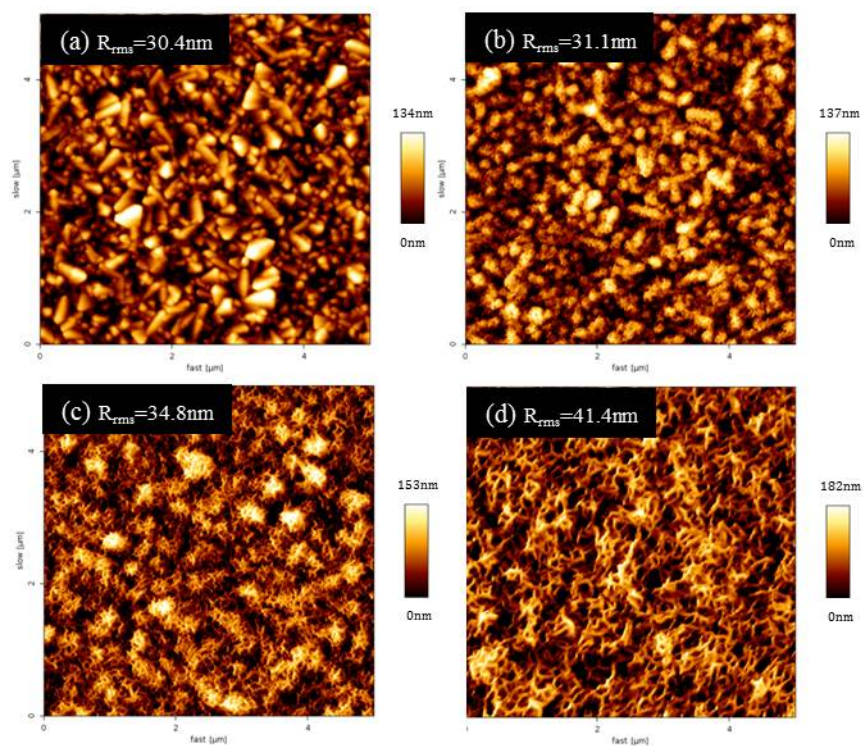


Fig. S2. AFM images of (a) bare-FTO, (b) 1-Ni(OH)₂/FTO, (c) 2-Ni(OH)₂/FTO and (d) 3-Ni(OH)₂/FTO

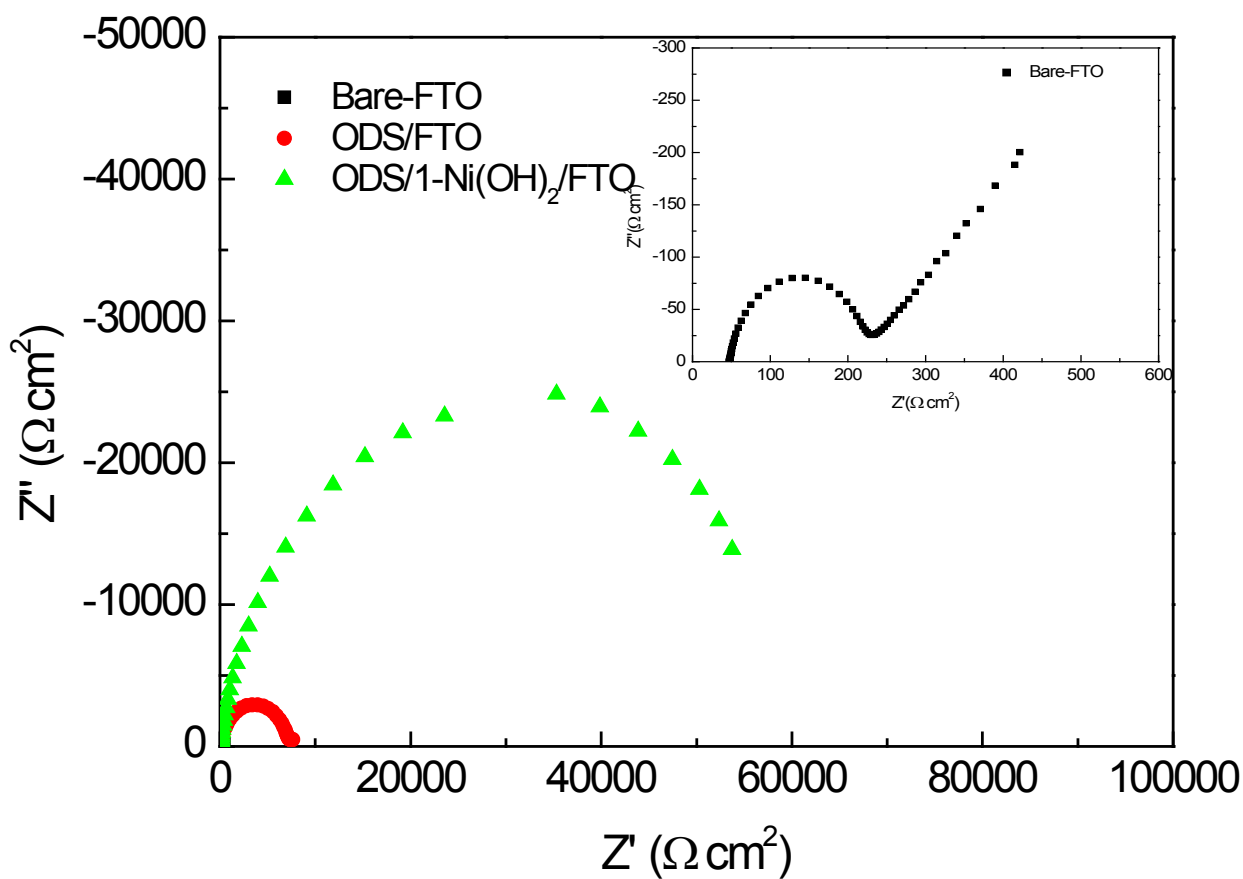


Fig. S3. AC impedance spectra of bare-FTO, ODS/FTO and ODS/1-Ni(OH)₂/FTO by using 2mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple as a probe, containing 0.2M KNO_3 as a supporting electrolyte. The AC impedance spectrum of bare-FTO is shown as an inset.

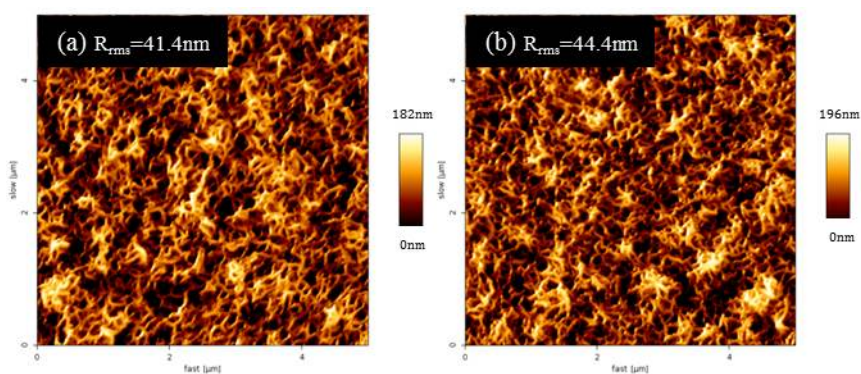


Fig. S4 AFM images of (a) 3-Ni(OH)₂/FTO and (b) ODS/3-Ni(OH)₂/FTO

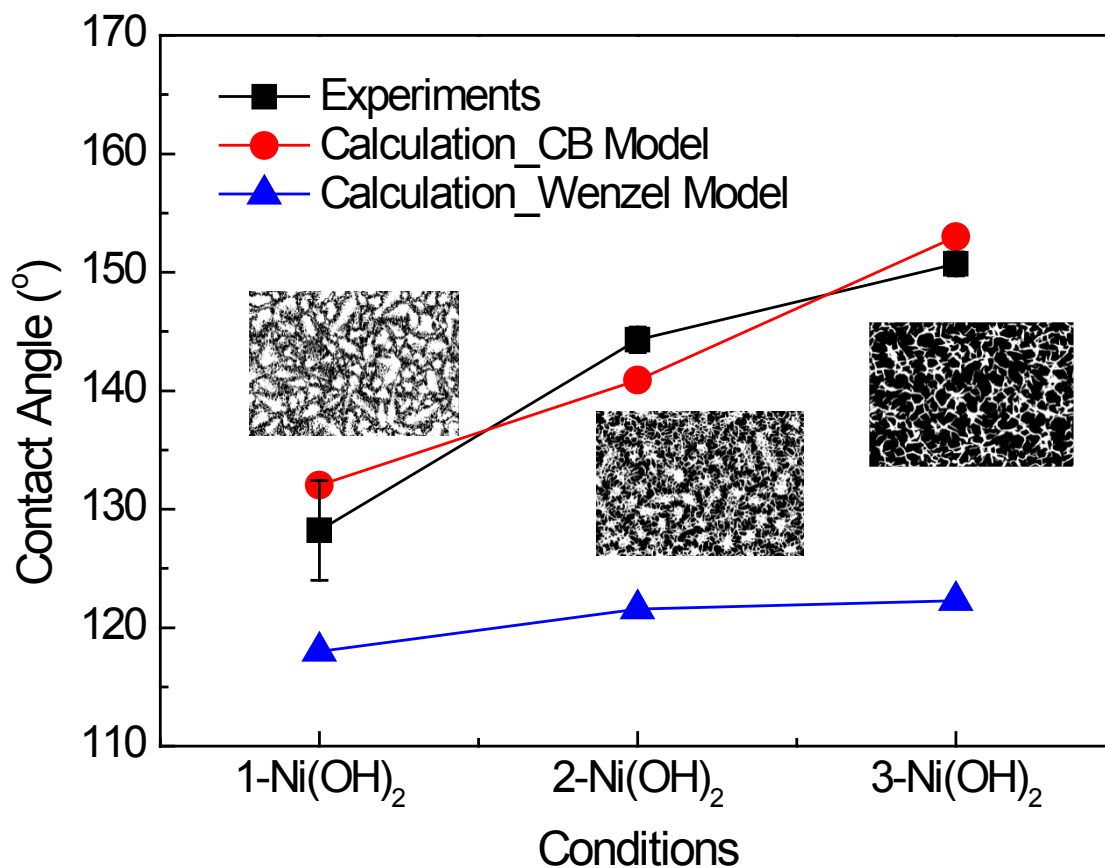


Fig. S5. Relationship between the WCAs of ODS/Ni(OH)₂/FTO and deposition conditions. (■)Experimental results from the goniometer, (●)calculated with f_{1V} values from SEM images, as shown in insets, based on the Cassie-Baxter's equation and (▲) calculated with predetermined roughness factor from **Fig. S2** based on the Wenzel's equation.

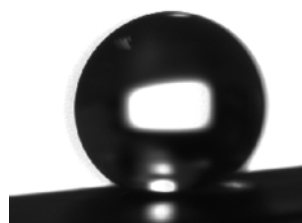


Fig.S6 Sliding angle of ODS/3-Ni(OH)₂/FTO.