

Supporting Information

The Design of Underwater Superoleophobic Ni/NiO Microstructures with Tunable Oil Adhesion

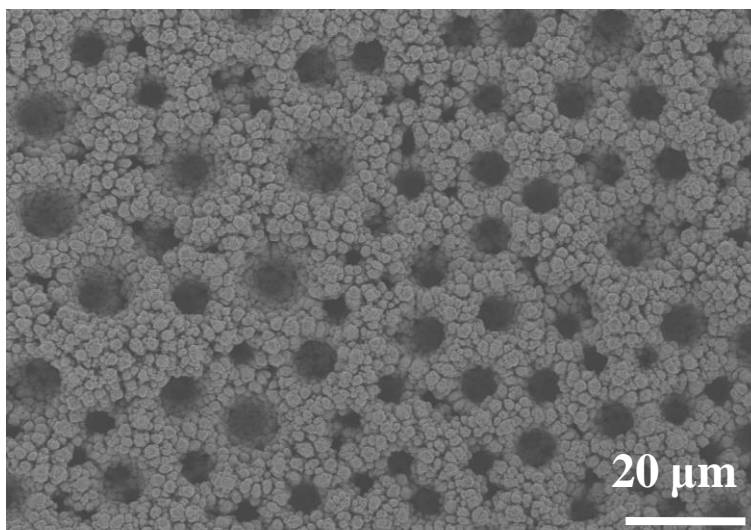


Figure S1. SEM image of the porous Ni film obtained after electro-deposition without heating treatment.

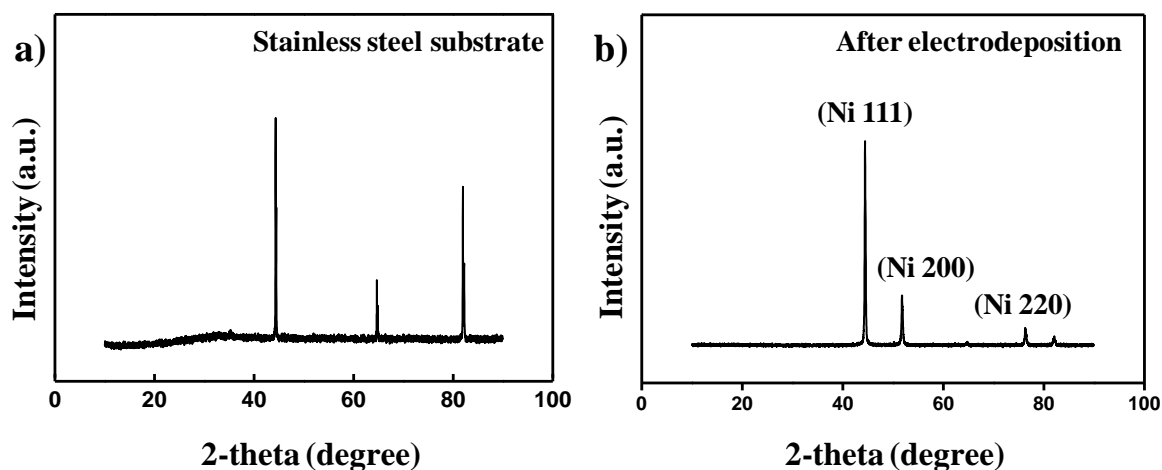


Figure S2. XRD results of stainless steel sheet (a) and porous Ni film without heating treatment (b), respectively.

X-ray diffraction data were collected using an X-ray diffractometer (D8 Advance, Bruker) with Cu K α radiation ($\lambda=1.5418$ Å). From these results, one can observe that after

electro-deposition, porous Ni microstructures have been produced on the stainless steel substrate.

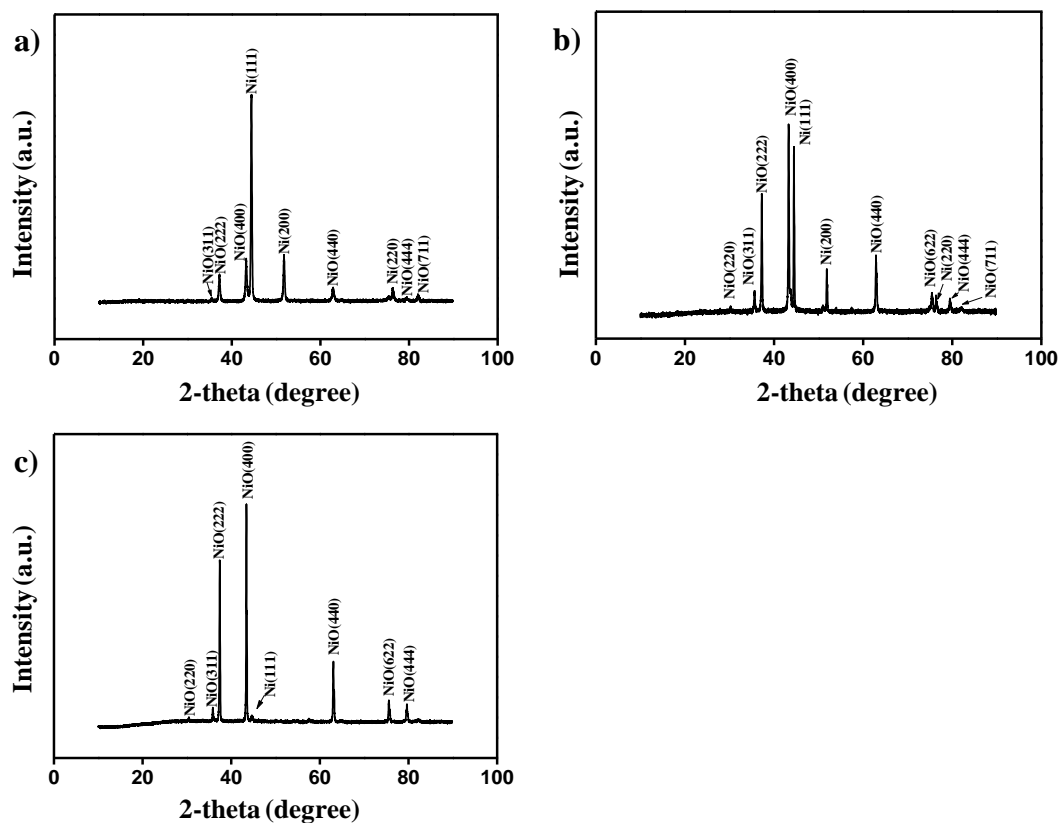


Figure S3. XRD patterns for surfaces after heating at different temperatures: (a) 500°C, (b) 900°C, and (c) 1100°C, respectively. It can be seen that after heating, all these surfaces are composed of Ni and NiO.

Discussion about surface microstructures variation at different heating temperatures

The surface microstructures variation can be explained by the sintering theory.^[1-4] When the surface is heated at relatively low temperature (500°C), only sintering necks between nanoparticles can be formed while the whole surface microstructures and size have no apparent variation. Therefore, as shown in Figure 1a and Figure S1, the film after heating at 500°C has the similar microstructures to the original film before heating treatment. When the heating temperature increases to 900°C, small nanoparticles would coalesce together to form

big particles and the total structures become denser. As shown in Figure 1b and 1d, the surface nanoparticles disappeared and irregular microblocks formed. Meanwhile, the average depth of the pores decreased compared with that on the surface S1. Further increase of the temperature would enhance the growth of particles and decrease of the interspaces spontaneously. As shown in Figure 1e and 1f, much bigger irregular microscale blocks formed and the pores disappeared.

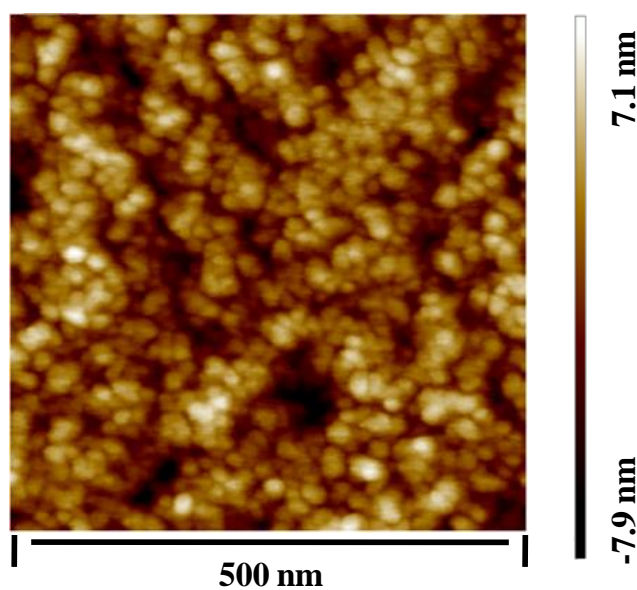


Figure S4. AFM image of the flat Ni/NiO surface.

The flat surface was prepared through the evaporation of Ni onto the flat glass substrate by using an evaporator (ZHD-300), and then heating at 350°C to obtain the Ni/NiO surface. By using an atomic force microscopy (AFM, Bruker, Dimension Icon), the surface roughness is measured to be 2.55 nm.

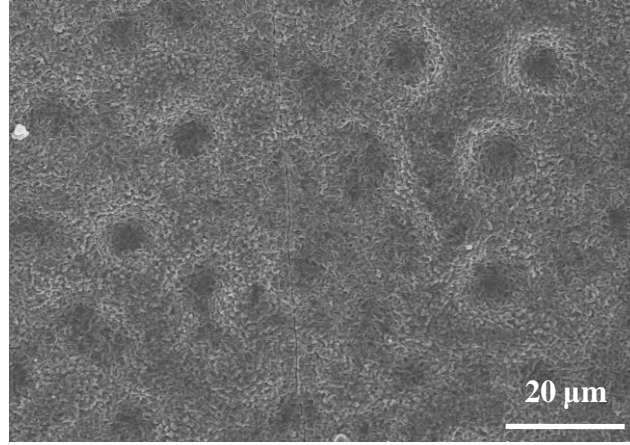


Figure S5. SEM image of the surface obtained at 1000°C.

As shown in Figure 5d, a sharp increase from about 8.2 μN to 60 μN between surface S2 and S3 is observed. We have tried to find a point between surface S2 (obtained at 900°C) and surface S3 (obtained at 1100°C), and prepared a surface obtained at 1000°C. Unfortunately, we find that the surface obtained at 1000°C has similar adhesion to the surface S2, and it is difficult to obtain a surface with in-between adhesive force between surface S2 and S3. As shown in Figure S5, similar to the surface S2, lots of microscale pits on the surface obtained at 1000°C can assist trapping water and result in the low adhesion to oil droplet, and the adhesive force is about 10.5 μN, which is similar to the surface S2. Therefore, in this work, three surfaces obtained at 500°C, 900°C, and 1100°C were selected to demonstrate the effect of surface microstructures on the oil adhesion in water.

Discussion about the underwater superoleophobicity on the microstructured surfaces:

As a comparison, the wetting performances on the flat Ni/NiO surface were also investigated. According to previous report,^[5] in the solid/water/oil three-phase system, the oil contact angle on a flat solid surface can be calculated from the following equation:

$$\cos \theta_{ow} = \frac{\gamma_{oa} \cos \theta_o - \gamma_{wa} \cos \theta_w}{\gamma_{ow}} \quad (1)$$

where θ_w , θ_o , and θ_{ow} are the contact angles of water in air, oil in air, and oil in water, respectively. γ_{ow} , γ_{wa} , and γ_{oa} are surface tensions of the oil/water, water/air, and oil/air interfaces, respectively. Herein, $\theta_w = 56^\circ$, $\theta_o = 6^\circ$ (Figure 3a), and according to the above equation, the theoretical $\theta_{ow} = 126^\circ$, which is approximate to the experimental result (130° , Figure 3b), indicating that the flat Ni/NiO surface is underwater oleophobic.

In this work, all of the as-prepared surfaces show underwater superoleophobicity, and the high oleophobicity can be ascribed to the enhanced effect of the surface microstructures. For surfaces S1 and S2, the high oil contact angles on the surface in water can be explained by the following modified Cassie equation:^[5,6]

$$\cos \theta'_{ow} = f \cos \theta_{ow} + f - 1 \quad (2)$$

Where f is the area fraction of the solid contact with oil droplet, θ'_{ow} is the oil contact angle on a rough solid surface in water, and θ_{ow} is the oil contact angle on a flat solid surface in water. Herein, $\theta_{ow} = 130^\circ$, for surfaces S1 and S2, θ'_{ow} are 162° and 158° , respectively (Figure 3b). According to the equation 2, f should be 0.137 and 0.203, respectively. These results indicate that most contact area under the oil droplet is the oil/water contact area, thus, the underwater superoleophobicity can be observed. Meanwhile, compared with surface S1, the surface S2 has a larger solid/oil contact area (the area fraction of the solid contact with oil droplet are 0.137 and 0.203 for surface S1 and S2, respectively). As a result, the surface S2 has a relatively high adhesion than surface S1.

For surface S3, the above equation would be unsuitable. The Cassie equation can explain the high oil contact angle (According to the above equation, on surface S3, f is 0.327, and the oil/water contact area is also large to result in the underwater superoleophobicity), but it cannot explain the high adhesive property. The above modified Cassie equation describes a composite contact interface, and the liquid droplet often can roll on the surface because the three-phase contact line is discrete,^[7] which is obviously contradictory with our experimental

result. Therefore, we believe that on the surface S3, the oil droplet resides in the Wenzel state, and the high oil contact angle can be explained by the following Wenzel equation:^[8]

$$\cos \theta''_{ow} = r \cos \theta_{ow} \quad (3)$$

Where θ''_{ow} is the oil contact angle on a rough solid surface in water, and θ_{ow} is the oil contact angle on a flat solid surface in water. r is defined as the ratio between the actual area of the rough surface and the geometric projected area, which is always larger than 1. Thus, for underwater oleophobic surface, the rough structures on the surface would enhance the surface oleophobicity and underwater superoleophobicity on the surface S3 can be observed. Meanwhile, in the Wenzel state, the liquid droplet contacts the solid substrate at all points, and a large contact area between oil droplet and solid surface can be formed, thus, the surface has a high adhesion to the oil droplet.

Reference

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