Preparation of a Superhydrophobic Ni Complementary Surface Using a Walnut Wood Template

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ABSTRACT: Ni is widely used in the field of corrosion protection because of its stability, hardness, and ductility. Inspired by the excellent hydrophobicity of walnut wood, imparted by its porous structure, we synthesized a morph-genetic, porous Ni sheet. A pyrolyzed walnut template was immersed in a Ni^{2+} solution, allowing Ni to be electroplated on the surface and to enter the skeleton’s pores. After calcination and surface modification, a template-free, low-surface-energy Ni sheet was obtained and accurately investigated by scanning electron microscopy and contact angle goniometry to evaluate its morphology and hydrophobicity. The results show that the Ni sheet inherited the complementary structure of the template, and, in turn, its water-repelling ability. We were able to measure contact angles as large as 150°, demonstrating that the new surface morphology endowed Ni with superhydrophobicity.

1. INTRODUCTION

Life on earth has undergone long periods of adaptation and development and has constantly evolved and been optimized to adapt to the changing environment. One of nature’s masterworks is the creation of hydrophobic surfaces, evolved to withstand a variety of conditions that benefit from water repulsion. In particular, superhydrophobic surfaces continue to amaze scientists, who constantly propose new strategies to reproduce their incredible properties, inspired by the potential industrial applications. Since these surfaces possess self-cleaning and anticorrosion properties, are resistant to freezing, and can reduce adhesion to water, special efforts have been made to endow metals with superhydrophobic properties.

Nickel is a magnetic transition metal with outstanding hardness, heat resistance, and corrosion resistance; properties preserved in its alloys as well. Superhydrophobic Ni surfaces have attracted increasing attention because of their potential applications in aircrafts, radar systems, missiles, tanks, ships, spacecrafts, and other military technologies. The key to producing a superhydrophobic Ni surface is to create a low-surface-energy material with a rough surface microstructure.

To date, several methods for preparing superhydrophobic surfaces have been reported, including electroplating," micro-molding and patterning, phase separation," etching, sol-gel, and electrostatic spinning techniques.10

Hardwood can be obtained from a multitude of angiosperm trees found in many regions of the world, and several varieties possess excellent hydrophobicity, because of their surface structure. In particular, walnut is a hardwood that contains pores of different sizes, a feature that was shown to impart superhydrophobicity.11,12

In a walnut wood cross section, many densely distributed pores can be seen, even by macroscopic observation. The underlying microstructures are shown in Figure 1: pores with different diameters are tightly packed on the wood’s surface, with large pores, i.e., those with a mean diameter of about 160–250 μm, present only in minority. Pores with diameters of 5–20 μm are arranged closely to form a honeycomb-like structure with a wall thickness of approximately 1 μm. This particular porous framework is an excellent air trap, and when water falls on the wood’s surface, the air layer acts as an effective barrier to water infiltration. Therefore, the honeycomb-like structure of walnut wood can be used as a template for designing superhydrophobic surfaces.

In this study, inspired by the novel concept of morph-genetic materials, a superhydrophobic Ni sheet was synthesized using walnut wood as a template.

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2. RESULTS AND DISCUSSION

2.1. Phase Identification. Figure 2a shows the X-ray diffraction (XRD) spectrum of a Ni sheet sample right after calcination and before fluoroalkyl silane (FAS) treatment. The peaks located at 44.5, 51.8, and 76.3° correspond to the (111), (200), and (220) planes of Ni (PDF# 04-0850 Ni), respectively, which confirmed that a Ni coating was successfully electroplated on the carbon skeleton. In addition, some low-intensity peaks can be observed at 37.2, 43.2, 62.9, and 75.4°, attributed to the presence of NiO (PDF# 47-1049, NiO). We speculate that NiO was formed by the oxidation of Ni coating during the high-temperature calcination phase. According to the XRD pattern, no other main components, besides Ni and NiO, were present on the sample’s protuberant surface.

Figure 2b shows the energy-dispersive spectrum (EDS) of a Ni sheet after FAS treatment. The EDS spectrum indicates that the main elements present were Ni, F, O, and a small amount of C. A large amount of F was present, indicating that FAS successfully bonded to the surface. In addition, the carbon signals were assigned to wood residues persisting on the surface even after the second aerobic calcination process.

2.2. Macrostructure and Hydrophobicity of the Prepared Nickel. To explore the effects of electroplating time on the morphology and properties of the surface, the samples were prepared with different electroplating times. Figure 3a–d shows the optical images of the samples fabricated using different electroplating times (0.5 h (a), 1 h (b), 1.5 h (c), and 2 h (d)), alongside their relative water droplets’ shape and contact angle (CA). The samples had dimensions of approximately 6 mm × 8 mm and displayed a green, rough
coating on the surface. Based on XRD results, the green coating was attributed to NiO accumulated during the calcination step. Moreover, the contact angles of the four samples were 144° (a), 146° (b), 150° (c), and 150° (d), highlighting the prominent hydrophobicity. Figure 3e shows the contact angle curve of four Ni sheets. This trend implies that the hydrophobic properties increased gradually with increasing plating time; particularly, the contact angles of the samples prepared in 1.5 and 2 h reached 150°, which locates these materials in the superhydrophobic range.

On the contrary, the contact angle of a smooth, FAS-modified Ni surface was only 115°, while the contact angle of the FAS-modified carbonized walnut was 150° (Figure 4).

Numerous studies have confirmed that the surface roughness of material is closely correlated to its hydrophobicity. The CA of the solid surfaces of the hydrophobic materials would increase if they are rough, i.e., a superhydrophobic surface can result from the increase of the roughness of the hydrophobic surface. Because our Ni sheet was synthesized using a walnut mold, its pillarlike structure mimics the wood’s porosity and is able to effectively repel water.

2.3. Microstructure of the Prepared Nickel. Figure 5a shows an SEM image of the Ni surface prepared using a plating time of 0.5 h. Two main sizes of vertical columnar structures were distributed on the sample’s surface. The larger columnar bulges had diameters of approximately 145–200 μm and were sparsely distributed on the surface, while small columnar bulges were densely distributed, with a mean diameter of 8–12 μm and a pore wall thickness of approximately 1 μm, as shown in Figure 5e. Note that the size and shape of the bulges on the Ni surface are consistent with the natural hollows in the walnut wood shown in Figure 1. This indicates that Ni electroplating was able to accurately replicate the porous structure of the natural walnut wood. Figure 5e also shows that the small-diameter columnar structures had uneven heights and that most columnar structures were hollow and tubular. We reasoned that these particular elements play an important role in imparting hydrophobicity, as indicated by the high overall contact angle of 144°, for the faculty to mimic walnut wood’s air-trapping ability.

Figure 5a–d shows low-magnification SEM images of nickel sheets prepared using electroplating times of 0.5, 1, 1.5, and 2 h, respectively, and proves that the complementary structure of the natural walnut template was accurately replicated (Figure 1). The high-magnification SEM images in Figure 5e–h help us evaluate the effects of electroplating time on microstructure and hydrophobicity. The cylindrical structures kept developing, and the walls of the tubes became thicker as the electroplating time increased. However, we observed that the ends of the tubes tended to gradually close for electroplating times longer than 1.5 h (Figure 5 g,h), yielding convex columnar structures. The tops of the columns were observed to be rough, which is beneficial to the hydrophobic properties. In summary, we observed that the microstructure of these Ni sheets changed with variations in electroplating time, which, in turn, determines the hydrophobic properties.

2.4. Adhesion Force of the Nickel Surface. To measure the dynamic water-repelling ability of the Ni surfaces at room temperature, 2 μL water droplets were contacted, pressed on, and detached from the four samples (Figure 6a). When the droplets were pressed on the Ni surfaces, they were observed to undergo three dynamic processes: shrinking, spreading, and bouncing. Eventually, the water droplets were completely detached from the sample, leaving a clean, liquid-free surface. Then, the adhesive force (AF) of each Ni sheet was measured using an electronic balance. We obtained the AF values of 13.1, 12.4, 11.4, and 11.3 μN for the samples electroplated for 0.5, 1, 1.5, and 2 h, respectively, which helped verify that the surfaces have low absorbable adhesion. Moreover, AF decreased gradually with increasing electroplating time, in accordance...
with the trends in hydrophobicity. As shown in Figure 6b, we also measured the roll-off angle of the nickel sample prepared with a plating time of 1.5 h to verify its superhydrophobic properties. The angle was approximately 6.9°, indicating excellent hydrophobicity.

3. SUMMARY

In this study, we proposed a method to synthesize superhydrophobic, morph-genetic Ni using walnut wood as a porous template. By means of electroplating, Ni sheets with complementary structures and similar sizes to the walnut wood molds were obtained. After removing the carbon template by aerobic calcination and modifying the Ni sheets with FAS, we characterized the obtained materials to evaluate the correlation between their hydrophobicity and morphology. We observed that the pores of the carbon skeleton led to the formation of bulges on the Ni sheets. Larger bulges, with a diameter of 145–200 μm, derived from Ni intercalation into large wood pores, while smaller bulges (8–12 μm) duplicated the smaller pores. SEM images showed that the size and distribution of the columnar protuberances on the Ni surface were basically consistent with the pore structure of walnut wood. Additionally, the surfaces of these Ni samples exhibited excellent hydrophobicity and low water adhesion after FAS modification. In other words, the porous structure, and the resulting hydrophobicity, of walnut was accurately and efficiently mimicked and used to improve the morphology and performance of the nickel sheets. This approach provides a feasible and straightforward route to prepare superhydrophobic metal materials imitating the microstructure of natural plants.

4. EXPERIMENTAL SECTION

4.1. Preparation of Ni Sheets. Walnut wood was first pyrolyzed in Ar atmosphere at 1000 °C for 1 h, with a heating rate of 2 °C min⁻¹, to prepare a carbonized walnut skeleton; according to a previous study on biomorphic superhydrophobic materials, this procedure allows wood to act as a more suitable template: during pyrolysis, cellulose decomposes, leaving a carbonized walnut skeleton with good electric conductivity, which can be used as a negative pole in electrochemical cells. Then, carbonized walnut was cut into 10 mm³ cubes and abraded using 800 grade silicon carbide paper.

Figure 7 shows the synthetic procedure that we adopted to obtain porous Ni sheets. First, a carbonized walnut template was dipped in a NiCl₂ solution ($n$Ni²⁺ = 0.5 mol L⁻¹) and electroplated as the cathode. A nickel plate was used as the anode. The current density of electrodeposition was 0.1 A cm⁻², and the reaction time varied from 0.5 to 2 h. Ni was able to grow on the wall of the pore during electroplating and gradually formed a porous coating, complementary to the mold. Then, the plated sample was placed in a muffle furnace and calcined at 1000 °C for 1 h in air to remove the carbon skeleton, yielding a structure characterized by hollow Ni pillars. Finally, the Ni sheet was soaked for 6 days in a mixture of fluoroalkyl silane (FAS, F-1060) and isopropanol to modify. As a result, this electrodeposition technique yielded a superhydrophobic Ni sheet with a complementary face.

4.2. Characterization. The surface morphology of the sheets was observed by a scanning electron microscope (Quanta 250FEG, Fisher Scientific). An X-ray diffraction spectroscope (D8 Advance, Bruker, Germany) was used to identify the materials’ crystal phases at a scan rate of 6° min⁻¹ and a step size of 0.02°. An energy-dispersive spectrocope (X-Maxn 80, Oxford Instruments, United Kingdom) was used to analyze the chemical elements on the samples’ surfaces. The superhydrophobic properties and the dynamic water-repelling abilities were characterized by contact angle measurements (JC2000D2, Shanghai Zhongchen Digital Technology, China) with 2 μL water droplets. The adhesive force of the surfaces was measured using an electronic balance.

Figure 7. Scheme of the fabrication process of a hydrophobic nickel sheet.
Self-cleaning Plant Surfaces.

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ABBREVIATIONS USED

FAS, fluoroalkyl silane; AF, adhesion force; SEM, scanning electron microscopy; XRD, X-ray diffraction; EDS, energy-dispersive spectrometry

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