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Preparation and corrosion resistance of superhydrophobic film by one-step electrodeposition

Wanyou Zhao ∗, Jun Li†, Yang Jin and Ming Chen

School of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, People’s Republic of China

∗ Author to whom any correspondence should be addressed.
E-mail: lijunlab@163.com

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Abstract

Superhydrophobic film with cauliflower-like structure was prepared on copper sheet by one-step electrodeposition method. The surface morphology and chemical composition of the superhydrophobic film were characterized by SEM, FTIR, XPS and contact angle measurements. Due to the cauliflower-like hierarchical structure and low surface energy, the as-prepared surface can reach up to a maximum contact angle of 158.3°, and the rolling angle is not more than 7°. Polarization curve was investigated using electrochemical workstation, and the as-prepared superhydrophobic surface showed improved corrosion resistance compared with bare copper.

1. Introduction

The research on superhydrophobic surfaces originated from the study of the surface structure and properties of lotus leaves and other animals and plants. These surfaces usually present a double-layer hierarchical structure, accompanied by a waxy coating [1–3]. Later, people defined a surface with a contact angle greater than 150° and a rolling angle less than 10° as a superhydrophobic surface, which has extremely strong water resistance and excellent self-cleaning properties. Through a lot of research, it is believed that the superhydrophobic properties are derived from the low surface energy chemical composition and rough surface physical structure, and the Cassie model and Wenzel model are proposed, which can interpret the relevance between surface roughness and contact angle [3–6]. Superhydrophobic surface has aroused the interest of researchers and has been applied in many research fields, such as anti-fogging [7], anti-scaling [8], hydrodynamic drag reduction [9], anti-icing [10], oil-water separation [11, 12] and so on.

Copper has become one of the most important metals in industry. The excellent thermal conductivity, electrical conductivity and mechanical durability enable copper to be used in engineering and electronic manufacturing, including power line, pipelines, heat exchangers, etc [13–15]. Meanwhile, the prevention of copper corrosion has also become an important issue due to the degradation and failure of device performance caused by corrosion [16, 17]. Due to the rise of superhydrophobic surface technology, many researchers have tried to apply superhydrophobic materials to metal anti-corrosion [18]. The air layer stored in the unique structure of superhydrophobic surface can reduce or avoid the contact of corrosive solution with metal substrate, thereby achieving the effect of anti-corrosion [19].

There have been many reports on anti-corrosion superhydrophobic coatings. Wang et al fabricated superhydrophobic film on copper foil from electrolyte solution mainly containing nickel chloride with choline chloride as crystal modifier by one-step electrodeposition approach [13]. Mohamed et al constructed superhydrophobic film by galvanostatic deposition using eggshell extract as additive and palmitic acid as low-surface-energy reagents. The addition of eggshell extract made the nickel film present a pine cone-like micronano structure [15]. Xu et al prepared superhydrophobic mesh by simply immersing copper mesh in the silver nitrate solution and then followed by modification with stearic acid solution [20]. All of the fabricated superhydrophobic films above exhibited superior corrosion resistance, indicating that constructing superhydrophobic coatings is an effective means to prevent or retard metal corrosion.

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In the past few decades, a variety of methods have been developed to fabricate superhydrophobic surfaces, such as sol-gel [21, 22], chemical etching [23, 24], chemical vapor deposition [25, 26], dip coating [27], laser ablation [28, 29], hydrothermal method [30], etc. Most of the methods require expensive equipment, harsh operating conditions or complex procedures, so it is difficult to apply to mass production [31]. In comparison, the electrochemical deposition method can be used to manufacture micro-nano structure under mild conditions simply and quickly, and the surface morphology and wettability can be controlled by changing the operating parameters such as voltage and current density [13]. Therefore, it is considered to be promising for large scale generation of superhydrophobic surfaces [31].

It is worth noting that electrodeposition method can be divided into multi-step and one-step method. The multi-step method is to construct the micro-nano structure by electrochemical deposition, then modify with low surface energy materials, but the modification time is often as long as several hours or even longer. However, one-step method does not require a separate modification step, and generally only takes a few minutes to tens of minutes to obtain superhydrophobic surface. In addition, the use of fluorosilane, chlorosilane and thiol as low surface energy modifier not only increases costs but also causes environmental pollution [28]. In summary, it is of great significance to choose cheap and environmentally friendly low-surface-energy reagents and to adopt one-step electrodeposition method.

Herein, superhydrophobic film on copper substrate was created with ethanol solution containing myristic acid and cobalt nitrate as electrolyte by one-step electrodeposition method. The effect of applied potential on the surface structure and contact angle was studied. We found that the surface morphology of the coating changed regularly with the voltage, which was the result of the acceleration of the crystal nucleus growth rate as the voltage increases. The change in morphology coincided with that of contact angle, confirming the importance of hierarchical structure for superhydrophobicity. The polarization curve of the sample was also obtained through the electrochemical workstation to investigate corrosion resistance of the superhydrophobic coating sample in the sodium chloride solution.

2. Experimental

2.1. Materials

Acetone was purchased from Chengdu Chron Chemicals Co., Ltd. Anhydrous ethanol was from Chengdu Jinshan Chemical Co., Ltd. Cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O] was obtained from Shanghai Macklin Biochemical Co., Ltd., China. Myristic acid (C₁₄H₂₈O₂) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. China. All chemicals were of analytical grade and used as received without further purification.

2.2. Sample preparation

A stainless steel plate was abraded with water sandpapers (from 400 to 1000 grades) and cleaned in distilled water. The stainless steel plate and polished Cu sheet were cleaned ultrasonically in acetone, ethanol, and distilled water respectively, and dried in atmosphere condition. Cobalt nitrate hexahydrate (0.02 M) and myristic acid (0.04 M) were added into ethanol under stirring to obtain a homogeneous electrolyte solution. Stainless steel plate was taken as anode and Cu sheet was used as cathode. The direct current (DC) voltage of 10–30 V was applied to two electrodes with a distance of 17.5 mm under room temperature. After 15 min of deposition, the final deposits were sequentially rinsed with ethanol and distilled water and then dried in an air condition. Finally, the sample was tested for chemical and superhydrophobic properties.

2.3. Characterization

Surface morphology of the samples was examined by scanning electron microscopy (SEM) (S-4800, Hitachi, Japan). The elemental composition was investigated by X-ray photoelectron spectroscopy (XPS) (AXIS Supra, Kratos, Japan). The chemical groups was characterized by Fourier transform infrared spectra (INVENIO® R, BRUKER, Germany). The water contact angle measurements were performed by a contact angle meter (DSA100, Kruss, Germany) for which 5 μl drops were dispersed on the surface of samples at ambient temperature. Young-Laplace fitting method is used to obtain the value of contact angles. At least three fresh points were measured for the same sample and the final result was averaged.

The chemical stabilization of samples was evaluated by electrochemical workstation (CS2350, Wuhan Corr Test Instrument Co., Ltd., China) at room temperature in a three electrode cell in which a platinum plate acted as counter electrode and saturated calomel electrode (SCE) as reference electrode. All measurements were performed in 3.5 wt% sodium chloride medium via linear voltammetry test at a scanning rate of 1 mV s⁻¹, and the exposed surface area of samples was 1 cm². Corrosion parameters such as corrosion potential (E_{corr}), corrosion density (I_{corr}), corrosion resistance (R_p) and corrosion rate were calculated from Tafel curves using CS studio (ver. 5.6) software.
3. Results and discussion

3.1. Surface morphology and wettability

Figure 1(a) shows the variation of contact angle (CA) of samples under different voltages and the picture of water droplets on the prepared surface. The average water contact angle of the processed surface obtained at a voltage of 10 V is 154.6°. The sample obtained at a voltage of 15 V gave an average CA of 155.0°. The average CA value obtained under 20 V and 25 V is 155.6° and 158.2°, respectively. When the voltage is increased to 30 V, the contact angle slightly increases to 158.3°, implying that there is no need to continue to increase the voltage, because the superhydrophobicity can no longer be greatly enhanced. The sample corresponding to the maximum contact angle has a rolling angle of 7°.

SEM images of the fabricated surfaces under different voltage was shown in figure 2. When the voltage is 10 V (figure 2(a)), the surface covering appears as spherical particles, mainly large particles with a diameter of 1.8–3.6 μm, and a small amount of small particles with a diameter of 0.45–0.85 μm. In the high magnification image (figure 2(b)), it can be more clearly observed that some smaller particles have gradually grown on the surface of the large particles. It is the structure formed by the accumulation of spherical particles that increases
the surface roughness of the substrate, and the interstice between the particles is also conducive to storing the air layer on the surface, thereby reducing the contact area between the droplets and the surface and making the droplets difficult to adhere. When the voltage is increased to 15 V (figure 2(c)), the surface shows clusters of spherical particles stacked on top of each other. The particles are larger compared with that of figure 2(a), and the diameter of the large particles is about 4–6 μm.

When the voltage is further increased, the surface morphology changes significantly, and the surface of the clusters presents a finer structure which is similar to a cauliflower (figures 2(e), (g), (i)). Comparing with the high magnification images, it can be found that the surface of the particles is smooth when the voltage is low (figures 2(b), (d)). When the voltage reaches 20 V (figures 2(f), (h), (j)), rough texture could be found on the surface of clusters. This is because as the voltage increases, the deposition rate becomes faster, and small particles continue to grow on the surface sites of large particles. When the voltage is high enough, the surface morphology of cauliflower-like clusters is formed. Combined with the changes of contact angle, the cauliflower-like surface morphology has a hierarchical size structure that is more complicated than the combination of particles of various sizes, which can more effectively reduce the contact area between the droplets and the surface and thus achieve a larger contact angle.

### 3.2. Chemical composition

Figure 3 illustrates the FTIR spectra of powder scraped from sample at 30 V (figure 3(a)) and myristic acid used in the experiment (figure 3(b)) to investigate the surface structures of as-prepared film. The wide absorption band observed between 3000 and 3700 cm⁻¹ appears in the figure 3(a) is assigned to –OH group. The strong
absorption peaks at 2918 and 2850 cm\(^{-1}\) are attributed to the C–H asymmetric and symmetric stretching of –CH\(_2\) groups \([32]\). There is a weak peak at 2955 cm\(^{-1}\) corresponding to the asymmetric in-plane C–H stretching of –CH\(_3\) group. It should be noted that there is no existence of –COO group at 1697 cm\(^{-1}\) in figure 3(a), whereas two strong adsorption peaks arise at 1541 cm\(^{-1}\) and 1404 cm\(^{-1}\), respectively. Hence, the new adsorption peaks may result from the asymmetric and symmetric stretches of –COO group. The peak at 1464 cm\(^{-1}\) is assigned to CH\(_2\) bending δ(CH\(_2\)) \([33]\). The narrow peak at 719 cm\(^{-1}\) originated from the in-plane rocking vibration of –(CH\(_2\))\(_n\) long carbon chains. The results above indicate that the film may be mainly composed of cobalt myristate and cobalt hydroxide, and the specific mechanism will be explained later.

XPS analyses were performed for superhydrophobic film at 30 V. As can be seen from the spectrum in figure 4(a), Co, C and O elements were observed. The peaks at 284.8, 285.5 and 288.5 eV in the C1s spectrum (figure 4(b)) were ascribed to C–C/C–H, C–O–C and O–C=O, respectively. The three peaks at 529.7, 531.8, and 532.8 eV in O1s spectrum (figure 4(c)) can be attributed to O—Co, C=O and C—O, respectively. The Co 2p spectrum (figure 4(d)) is resolved into 4 main peaks, the peaks at 780.6 and 796.4 eV belong to Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\) respectively, and the peaks at 782.0 and 797.9 eV can be attributed to Co(OH)\(_2\) species. In addition, there are two satellites peaks at 785.3 and 802.7 eV.

Based on the above results, the electrodeposition process is illustrated in figure 5. NO\(_3^-\) combines with water molecules and free electrons near the cathode to form OH\(^-\), which then react with Co\(^{2+}\) to form Co(OH)\(_2\). Besides, Co\(^{2+}\) also react with myristic acid to form Co[CH\(_3\)(CH\(_2\))\(_{12}\)COO]\(_2\). Moreover, free H\(^+\) ions combine with free electrons to form H\(_2\). It has been reported that the generation of hydrogen is conducive to the formation of loose micro-nano structure, thereby promoting superhydrophobicity \([34]\). The reaction process is shown in equations (1)–(4):

\[
\begin{align*}
\text{NO}_3^- + 7\text{H}_2\text{O} + 8\text{e}^- & \rightarrow \text{NH}_4^+ + 10\text{OH}^- \\
\text{Co}^{2+} + 2\text{OH}^- & \rightarrow \text{Co(OH)}_2 \\
\text{Co}^{2+} + 2\text{CH}_3(\text{CH}_2)_{12}\text{COOH} & \rightarrow \text{Co[CH}_3(\text{CH}_2)_{12}\text{COO}]_2 + 2\text{H}^+ \\
2\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2
\end{align*}
\]

3.3. Corrosion resistance studies

The electrochemical corrosion of bare copper and superhydrophobic films in 3.5 wt% sodium chloride aqueous were observed. All the samples were immersed in solution for 2 h before the experiment to ensure that the samples attained a stable state in the solution. The Tafel characterization analysis is illustrated in figure 6 and the relevant polarization parameter values are listed in table 1. The corrosion current density, corrosion potential and corrosion rate are obtained using the Tafel extrapolation method. The polarisation resistance (R\(_p\)) was calculated based on Stern-Geary equation.
It is generally believed that, from the perspective of kinetics, metals with higher corrosion current density are tend to be corroded, while it is just the opposite for corrosion potential\cite{35}. As could be seen in figure 6, all the superhydrophobic samples exhibit lower $I_{corr}$ and corrosion rate compared with copper, indicating that the superhydrophobic films significantly enhanced the corrosion performance. Sample formed at 30 V exhibits the most excellent corrosion resistance with the lowest corrosion current density of $2.04 \times 10^{-8} \text{A cm}^{-2}$ and the highest corrosion potential of $-0.222 \text{V}$. As for the sample obtained at 10 V and 15 V, although the corrosion potential is lower than that of copper, the corrosion current and corrosion rate are also lower. In other words, a lower corrosion potential does not necessarily mean better performance of corrosion resistance. Comparing other superhydrophobic samples (20 V, 25 V and 30 V) with bare copper, we can found that the corrosion potential of superhydrophobic samples is only slightly increased yet the corrosion current density is significantly reduced. The corrosion current density of superhydrophobic sample at 30 V decreases by two orders of magnitude compared with copper.

4. Conclusions

Using safe and environmentally friendly low-surface-energy agent, a super-hydrophobic surface is manufactured on copper substrate by a simple and rapid method, which is low cost and easy to operate, and is expected to be applied to industrial production of superhydrophobic surfaces. The surface morphology of films obtained under different voltages present different characteristics. The cauliflower-like surface morphology can be formed under a higher voltage. This hierarchical structure enables the surface voids to store air and thus effectively reduces the solid-liquid contact area, and finally exhibits excellent hydrophobicity. The maximum surface contact angle could reach up to $158.3^\circ$, and the sliding angle is no more than $7^\circ$. The results of FTIR and XPS spectra analysis show that the main components of the coating are cobalt myristate and cobalt hydroxide.
and the specific mechanism is explained accordingly. The electrochemical test results show that superhydrophobic coating could promote the reduction of corrosion current and corrosion rate, while it does not necessarily increase the corrosion potential. Nonetheless, the value of corrosion potential only means the tendency of corrosion in thermodynamics and cannot evaluate the actual corrosion process.
Table 1. The electrochemical parameters of bare Cu and SHP surface by polarization curves during immersion in 3.5 wt% NaCl aqueous.

| Sample | Ecorr(V) | Icorr(A/cm²) | B2(mV) | B1(mV) | CR(mm/y) | Rs(Ω·cm²) |
|--------|---------|-------------|--------|--------|----------|-----------|
| Bare   | -0.259  | 8.68 × 10⁻⁶ | 74     | -153   | 1.02 × 10⁻¹ | 2.69 × 10³ |
| 10V    | -0.280  | 1.20 × 10⁻⁶ | 213    | -154   | 1.39 × 10⁻² | 3.28 × 10⁴ |
| 15V    | -0.260  | 2.35 × 10⁻⁷ | 97     | -130   | 2.76 × 10⁻³ | 1.08 × 10⁵ |
| 20V    | -0.247  | 8.12 × 10⁻⁷ | 88     | -112   | 9.52 × 10⁻³ | 2.70 × 10⁴ |
| 25V    | -0.255  | 3.60 × 10⁻⁸ | 111    | -104   | 4.22 × 10⁻⁴ | 6.96 × 10⁵ |
| 30V    | -0.222  | 2.04 × 10⁻⁸ | 100    | -105   | 2.40 × 10⁻⁴ | 1.12 × 10⁵ |

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

ORCID iDs

Wanyou Zhao  https://orcid.org/0000-0002-4611-632X
Jun Li  https://orcid.org/0000-0002-5823-9837

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