A sample hydrothermal method for preparing durable Ni$_3$S$_2$ superomniphobic surface

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Abstract. With the development of surface science and bionics, the wettability of solid surfaces has drawn a broad attention. A simple hydrothermal reaction was used for the preparation of Ni$_3$S$_2$ coating with nanowires structure. Then the surface modified by tetradecanoic acid displayed an excellent repellence to water, glycerol and ethanol solutions. The stability of the Ni$_3$S$_2$ superomniphobic surface was investigated, finding that the superomniphobic surface owned a great resistance to the tape-peeling and air environment. The method for preparing Ni$_3$S$_2$ superomniphobic coating is simple and economical, which has an advantage in future application in self-cleaning and oil-water separation.

1. Introduction

The wettability is an important feature of solid surfaces and plays an important role in industrial production and daily life [1]. The “lotus effect” [2], an extreme wetting phenomenon was proposed by Barthlott et.al, which meant that the water droplets could maintain a complete spherical shape on the lotus leaf and remove the dust by rolling off from its surface. The special wetting phenomenon was defined as superhydrophobic. The contact angle is a critical parameter to evaluate the wettability, both the contact angle more than 150° and sliding angle less than 10° could be considered as a superhydrophobic surface [3-4]. Superhydrophobic surface has become a hot issue and attracted a wide attention for multifarious applications due to its excellent properties, such as corrosion resistance [5], anti-icing [6], self-cleaning [7], drag reduction [8], oil-separation [9] etc. In general, the wettability of superhydrophobic surface is primarily controlled by both the low surface energy and coarse structure [10].

The transition metal nickel performs well in resisting corrosion. If a superhydrophobic surface is constructed on the nickel substrate, it will further reduce the adhesion of contaminants and improve the corrosion resistance. However, the water contact angle on the smooth nickel surface modified by the low surface energy substance was only 120.45°. Therefore, the key to obtain superhydrophobicity on nickel substrate is to artificially construct coarse microstructures.

In this paper, a facile and inexpensive hydrothermal reaction was used to prepare Ni$_3$S$_2$ microstructure on the nickel surface and subsequently modified with tetradecanoic acid. Meanwhile, a tape-peeling test was carried out to evaluate the bond strength of Ni$_3$S$_2$ coating to the substrate. The variation of water contact angles with storage time was recorded to investigate the stability of Ni$_3$S$_2$ superhydrophobic coating.
2. Experimental

2.1 Materials
The experiment was carried out on pure nickel and the ingredients are listed in Table 1. All of the chemical reagents, including anhydrous ethanol, NiSO₄, TAA, NaOH, CTAB, HCl, tetradecanoic acid were purchased from Sinopharm Chemical Reagent Co., Ltd.

Table 1. The ingredients of pure nickel.

| Name | Ni   | Cu     | Fe    | Co    | C     | Si     | Pb     | S     |
|------|------|--------|-------|-------|-------|--------|--------|-------|
| Nickel | Balance | 0.0029 | 0.0026 | 0.0019 | 0.0018 | 0.0018 | 0.0006 | <0.0005 |

2.2 Preparation of superhydrophobic coating
A facile hydrothermal method was used to fabricate superomniphobic coating. To begin with, the nickel substrates were polished by water sandpaper to 2000#. Then the nickel substrates were ultrasonically cleaned with deionized water and absolute ethanol for 10 min to remove surface contaminants. A 60 mL ethanol solution including 0.1 g NiSO₄, 1.8 g NaOH, 1 g CTAB and 0.22g TAA stirred for 10 min was transferred into a polytetrafluorethylene-lined stainless steel autoclave. Subsequently, a nickel substrate was placed into the solution. The autoclave was heated at 180 ℃ for 10 h and naturally cooled to room temperature after the reaction. The resulting sample was flushed with sufficient anhydrous ethanol before dried at 60 ℃ for 2 h. Subsequently, the as-prepared sample was modified by tetradecanoic acid solution for 12 h. Then a superhydrophobic surface was obtained after drying at 35 °C for 6 h.

2.3 Characterizations
The morphology of the coating was observed by scanning electron microscope (JEOL JSM-7200F). And the X-ray diffraction (XRD) patterns were recorded via a diffractometer (XRD, X’Pert PRO MPD, PANalytical). The contact angles were measured by a dynamic/static contact angle meter (SL200B, USA, KINO).

3. Results and discussion

3.1 Wettability
The contact angles were measured on sample surface to characterize its wettability. It was worth noting that modified coating was significantly resistant to water droplets (3μL) and the contact angle was up to 162.51°. Once the sample was tilted, the water droplets would roll off from the surface. Glycerol droplets (3μL) also remained spherical shape on its surface and the contact angle was 154.94°. In order to further investigate the lyophobicity of the coating, the contact angles were measured by ethanol aqueous solutions of different volume ratios. The measurement results are shown in the Table 2. As the proportion of ethanol reduced, the contact angle gradually increased. The low surface energy played an important role in the lyophobicity [11]. The effect of coating surface topography on superomniphobicity will be discussed in the next section.

Table 2. The contact angles of different volume ratios of ethanol and water.

| Volume ratios of ethanol and water | Contact angles/° |
|-----------------------------------|------------------|
| 1:1                               | 125.79±2.11      |
| 1:2                               | 148.29±2.27      |
| 1:3                               | 158.91±0.99      |
| 1:4                               | 161.35±0.42      |
| 1:5                               | 162.79±0.95      |
3.2 Chemical composition and topography of Ni$_3$S$_2$ coating
As the XRD patterns depicted in Figure 1, no impurity existed other than the nickel and heazlewoodite Ni$_3$S$_2$. And the diffraction peaks were sharper that displayed a nice crystallinity. The topography of substrate and Ni$_3$S$_2$ coating is shown in the Figure 2. Some lamellar bulges could be noted on the substrate (Figure 2(a)). Then the substrate was covered with dense Ni$_3$S$_2$ nanowires after hydrothermal reaction (Figure 2(b)). Therefore, a large number of grooves formed between the nanowires to store air. The air provided a barrier to stop droplets from filling grooves and the droplets could maintain a complete spherical shape. Instead, few grooves existed to form air layer resulting that the substrate was easily wetted.

![Figure 1. The XRD patterns of superomniphobic surface.](image)

![Figure 2. The topography of nickel (a) and superomniphobic coating (b).](image)

3.3 Stability of Ni$_3$S$_2$ superomniphobic coating
The stability of Ni$_3$S$_2$ superomniphobic coating was evaluated by withstanding the mechanical damage and air environment. The tape-peeling test was performed to evaluate the mechanical stability and the tape was replaced every 10 times to ensure its adhesiveness. A variation of contact angles is displayed in Figure 3(a). There was no obvious variation of contact angles and the surface maintained a higher contact angle even after 100 times. This could root from the in-situ growth of Ni$_3$S$_2$ nanowires forming strong bond with the substrate. Moreover, superomniphobic samples were placed in the air environment (the city, Qingdao) for 60 days, the contact angles were also little changed as the Figure 3(b) shown. This result mainly owned to the formation of air layer which prevented ions and H$_2$O molecule in the atmosphere from damaging the substrate.
4. Conclusion
In summary, the Ni$_3$S$_2$ coating with nanowires structure was fabricated via a simple and inexpensive hydrothermal reaction method. A stable superomniphobic surface was obtained by the followed modification with tetradecanoic acid. The droplets of water, glycerol and ethanol solutions could keep spherical shapes on the coating surface even the water contact angle was up to 162.51°. Besides, the superomniphobic surface could withstand the destruction from tape-peeling and air environment. The ability that resists the wetting by droplets provides a new thought for further surface cleaning and anti-corrosion.

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