Fabrication of superhydrophobic Fe$_2$O$_3$/Fe$_3$O$_4$ composite surface on N80 substrate

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Abstract. Fe$_2$O$_3$/Fe$_3$O$_4$ compositd film with micro-nano structures is prepared on the surface of N80 steel. The Fe$_2$O$_3$/Fe$_3$O$_4$ compositd film after modification with stearic acid shows great superhydrophobicity with a water contact angle of 157.3° and sliding angle of 8.1°. Furthermore, the superhydrophobic Fe$_2$O$_3$/Fe$_3$O$_4$ compositd film can keep anti-wettability when it is immersed in the water and make water droplets keep sphere on it. Furthermore, the superhydrophobic surface also shows excellent self-cleaning property. Our work finds that annealing in the atmosphere after egg white burning can produce nanoneedle structures perpendicular to the micro-octahedron, which plays a significant role to make micro-nano hierarchical structures for Fe$_2$O$_3$/Fe$_3$O$_4$ composite film.

1. Introduction

Superhydrophobic surface has attracted much attention due to its anti-icing, self-cleaning, anti-corrosion and so on [1]. It is easy to identify from the contact angle larger than 150° and sliding angle less than 10°. The superhydrophobic surface is decided by the hierarchical structures and the low surface energy material. The morphology structure is an important role to affect the surface properties. In our previous researches, it found the annealing process is an effective way to enhance the micro-nanostructures [2,3]. Also, enormous work has been reported about annealing treatment to improve the wettability [4-6]. For example, Wu et. al made the superhydrophobic surface on the Zn substrate by etching and annealing treatment. The nanometer needle-like structures exhibited micron-sized protrusions to formation hierarchical structures, which induced the superhydrophobic surface with the water contact angle of 160° [7]. Ngo et. al found the laser-textured surface of SUS304 annealing in over for low temperature could improve the wettability. The surface on SUS304 displayed hydrophilic after laser texturing. However, after low temperature annealing, the laser-texturing surface transformed to superhydrophobic [8]. Kim et. al synthesized the nanoporous BiVO$_4$ surface by electrochemical deposition and thermal treatment. They found the hydrophilic BiVO$_4$ surface became hydrophobic after annealing in N$_2$ [9]. So, it can be seen that annealing is an easy treatment method to improve the surface wettability.

Herein, we report a new discovery to prepare the superhydrophobic Fe$_2$O$_3$/Fe$_3$O$_4$ compositd surface by hydrothermal treatment and annealing process on N80 steel. The hierarchical structures were obtained after annealing in the atmosphere after the egg white burning. The influence of the annealing time on the surface morphology for the superhydrophobic sample is investigated. The results suggest that appropriate hierarchical structure is a significant factor for the superhydrophobicity after modifying with stearic acid.
2. Experimental

2.1. Materials
The N80 (supplied by Yangzhou Keli environmental protection equipment Co., Ltd) sample was a wafer with a diameter of 14.5 mm. The 100 ml Teflon-lined stainless-steel autoclave (supplied by Xi’an Yi Chuang Laboratory Instrument and Equipment Co., Ltd.) were used. The egg was bought from the supermarket and only the egg white was used. The chemical reagents used in our work include ethylenediamine (C₂H₈N₂, EDA), stearic acid (C₁₈H₃₆O₂) and ethanol. All of them were analytical grade, purchased from Sinopharm, and used without further purification.

2.2. Experimental Procedure
In a typical procedure, the N80 steel was cleaned by acetone, ethanol and distilled water for a while and dried in air. The ethylenediamine aqueous solution (3.75 M, 20 ml) and N80 steel were placed into a 100 ml Teflon-lined stainless-steel autoclave, and then heated to 165 °C for 7 h in oven. When it cooled down, the black as-prepared sample was obtained after cleaning by ethanol. About 3 ml egg white was taken into the tube furnace under 550 °C for 30 min (heat rate for 5 °C/min). After that, an annealing process was carried out for the as-prepared sample at 550 °C for different annealing time (0.5, 1.5, 2 and 2.5 h) under the atmosphere after egg white burning. Finally, the annealing sample modified with 8 Mm stearic acid ethanol solution for 5 h at room temperature. The procedure for the hydrophobic samples is shown in Figure 1.

![Figure 1. Schematic of the procedure on the preparation of the hydrophobic sample.](image)

2.3. Characterization
X-ray diffraction (XRD) patterns of the samples were recorded by a D8 ADVANCE X-ray diffractometer under a scanning rate of 0.2 per second in the 2θ range from 20 to 80°. Morphologies of the sample were observed by a field emission scanning electron microscope (FESEM, ZEISS SIGMA). The water contact angle and sliding angle were studied by a JinHe JY-PHb contact angle measurement device. And each sample is selected in five different places for measurement with about 10 µL water.

3. Results and Discuss

3.1. XRD Analysis
The XRD patterns of the as-prepared sample and different annealed samples are shown in Figure 2. For the as-prepared sample (Figure 2a), the diffraction peaks match well with the phase for Fe₃O₄ (JCPDS card No. 19-0629) and Fe (JCPDS card No. 06-0696), which means the Fe₃O₄ film is obtained.
after the hydrothermal treatment. For the different annealed sample, it can be easy to find that all the diffraction peaks of them are similar, mainly Fe$_3$O$_4$, Fe$_2$O$_3$ (JCPDS card No. 33-0664) and Fe. The emergence of the Fe$_2$O$_3$ phase indicates that the Fe$_3$O$_4$ may be oxidized during the annealing process the atmosphere after egg white burning. Moreover, from the (104) diffraction peaks of Fe$_2$O$_3$ in Figure 2b-c, it can be found that the diffraction peaks of annealed samples with annealing time of 2.5 h are stronger than those of other annealed samples. This implies the crystallinity of Fe$_2$O$_3$ is higher than that of other annealed samples. In summary, the Fe$_2$O$_3$/Fe$_3$O$_4$ composite phase is obtained after annealing process.

Figure 2. XRD patterns of (a) the as-prepared sample and the annealed sample at different annealing time (b) 0.5 h (c) 1.5 h (d) 2 h and (e) 2.5 h.

### 3.2. SEM Analysis

The morphologies of the as-prepared sample and annealed samples are studied by SEM, showing in Figure 3. For the as-prepared sample, a smooth surface of the micro-octahedron can be seen (Figure 3a). The significant changes appear when the as-prepared sample is annealed in the atmosphere after egg white burning. When the annealing time is 0.5 h, it can be found that the surface of the micro-octahedron becomes rough and some white dots can be observed (Figure 3b). When the annealing time is extended to 1.5 h, some needle strips appear (Figure 3c). In contrast, a large number of needle strips emerge and cover the entire surface of the micro-octahedron when the annealing time reaches at 2 h (Figure 3d). Furthermore, the needle strips continue to grow and become longer when the annealing time is 2.5 h (Figure 3e). From the XRD analysis, the micro-octahedrons belong to Fe$_3$O$_4$ and the needle strips match with Fe$_2$O$_3$. The process of the needle strip growth is also consistent with the crystallinity of Fe$_2$O$_3$ in XRD analysis.

Figure 3. SEM images of (a) the as-prepared sample and annealed sample at different annealing time (b) 0.5 h (c) 1.5 h (d) 2 h and (e) 2.5 h.
3.3. Wettability Analysis

The hydrophobic samples are obtained after the annealed samples modify with stearic acid. The contact angles and sliding angles of them are shown in Figure 4. It can be found that the water contact angles of the hydrophobic samples under different annealing times are higher than 150°. Moreover, the hydrophobic sample under annealing for 2 h performs better than others, the contact angle of which is 157.3°. In general, a contact angle greater than 150° and a sliding angle less than 10° are the state of superhydrophobicity. It can be found that the sliding angles among the hydrophobic samples are different. Only the sliding angle of the hydrophobic sample under annealing for 2 h performs 8.1°, and others are higher than 10°. So the hydrophobic sample under annealing for 2 h shows great superhydrophobicity. The micro-nano hierarchical structures and low energy surface material decide the superhydrophobicity.

![Figure 4. Optical image of water contact angles and sliding angles of the hydrophobic samples under different annealing time (a) 0.5 h (b) 1.5 h (c) 2 h and (d) 2.5 h.](image)

3.4. Anti-wettability Behaviors

Owing to the great anti-wettability of the superhydrophobic sample, the wettability behaviors preform against water, which are shown in Figure 5. For the immersing test, the surface of the superhydrophobic sample is shine, that is because the air cushions exist between the solid surface and water to prevent wetting of the surface. The water droplets on the superhydrophobic sample remain spherical, showing in Figure 5b. Meanwhile, for the self-cleaning test (Figure 5c), the chalk crumbs on the superhydrophobic sample are easily carried away by falling droplets of water. All above, the superhydrophobic sample shows great non-wettability.

![Figure 5. The wettability behaviors of the superhydrophobic sample in (a) immersing test (b) water droplet standing test and (c) self-cleaning.](image)
4. Conclusion
In this paper, a new method of preparing Fe$_2$O$_3$/Fe$_3$O$_4$ composite film is proposed. The special hierarchical structures, micro-octahedron and nanoneedle, are prepared by hydrothermal treatment and annealing process. The nanoneedle structures perpendicular to the micro-octahedron are obtained when the as-prepared samples annealed in the atmosphere after egg white burning. It can be found that the different annealing times have an important effect on the morphological structures. After modification with stearic acid, the annealing samples become hydrophobic. Especially, the hydrophobic sample with annealing for 2 h displays better, which preforms superhydrophobic with contact angle of 157.3° and sliding angle of 8.1°. Furthermore, the water droplets on the surface of the superhydrophobic sample can stay sphere. It also shows excellent anti-wettability in the water and great self-cleaning. This work provides new ideas and references for the preparation of micro-nanostructures in the future superhydrophobic surface.

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