

Superhydrophobic iron material surface with flower-like structures obtained by a facile self-assembled monolayer

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Abstract A simple and economical route based on a K_2CO_3 mediated process was developed to synthesize three-dimensional (3D) flower-like Fe_3O_4 micro/nanoflakes on the surface of iron plates by a direct in-situ hydrothermal synthesis method. The prepared micro/nanoflakes were characterized by X-ray diffraction and scanning electron microscopy. It was found that the width of the nanoflakes ranges from 50 to 100 nm, and the length of the flakes is about 3 μm . The morphology of Fe_3O_4 nanostructures can be tuned from simple isolated nanoflakes to the ordered 3D flower-like shape by increasing the reaction temperature. The wettability of the surface with 3D flower-like micro/nanoflakes was changed from hydrophilicity to superhydrophobicity by chemical modification with vinyl triethoxy-silane. The static contact angles for water on both of the modified surfaces were larger than 150° , which was closely related to the chemical modification and hierarchical structure. Furthermore, the surfaces retained good superhydrophobic stability in long-term storage as well, which should be critical to the application of iron materials in engineering.

1 Introduction

Superhydrophobic surfaces, inspired by water-repellent surfaces in nature, have attracted a great deal of interest for fundamental research and practical applications [1, 2]. The most well-known superhydrophobic surfaces are lotus leaves. The surfaces of lotus leaves consist of microscale

epidermal cells covered by nanoscale epicuticular wax crystals. The combination of surface roughness and wax coating renders the lotus leaves superhydrophobic with a water contact angle (WCA) of about 160° . Therefore, research on superhydrophobic surfaces has been motivated by mimicking nature on one hand [3]. The superhydrophobic surfaces are usually fabricated via two approaches: creating micro-nanostructures on intrinsically hydrophobic substrates, or chemically modifying the micro-nanostructured surfaces (either hydrophobic or hydrophilic) by materials with low surface free energy [4]. Many elegant methods, such as template synthesis [5], electrochemical deposition [6], laser structuring [7, 8], and so on [9, 10], have been developed to construct micro-nanostructures on a hydrophilic substrate. Until now, many methods have been reported for constructing superhydrophobic surfaces by mimicking the surface of lotus leaves. Some scientists have demonstrated fabrications of artificial superhydrophobic surfaces via lithography-based etching [11], deposition techniques [12], and template-based extrusion [13, 14]. Nevertheless, most of these reported approaches are costly thanks to rigorous experimental conditions, such as clean-room facilities, or are restricted in certain applications.

A simple chemical composition method for a substrate coated with copper using n-tetradecanoic acid solution was reported by Jiang and coworkers [15], but the procedure took a long time and the type of substrate was restricted. Relatively easy chemical etching methods were presented by Shen and Liu for polycrystalline metal and for aluminum and its alloys, respectively [16, 17], but some engineering materials such as iron, copper alloy, and titanium alloy cannot be etched effectively by dislocation enchants and basic solutions. Since these alloys have diverse technological applications in the marine, auto, aviation, and space industries, superhydrophobicity (self-cleaning and anticorrosive prop-

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erties) will greatly extend their applications as engineering materials [18]. Therefore, a highly effective, inexpensive, simple, and convenient to operate method that would be very advantageous for industrial large-scale production is needed.

Herein, we present a direct in-situ hydrothermal synthesis method for constructing three-dimensional (3D) flower-like micro/nanoflakes on an iron plate surface. The micro-nanostructure of the surface has been readily controlled by adjusting the reaction temperature and the concentration of precursor. After chemical modification with vinyl triethoxysilane (VTS), the resultant surface covered by flower-like micro/nanoflakes has a high water contact angle of about 157° and a low sliding angle (SA) of about 1° .

2 Materials and methods

The iron plates with a size of $40\text{ mm} \times 40\text{ mm} \times 0.5\text{ mm}$ (Sinopharm Chemical Reagent Co. Ltd., Shanghai, P.R. China; purity 99.8%) were ultrasonically cleaned in ethanol and deionized water for about 30 min, respectively, followed by immersion into Teflon autoclaves filled with 40 ml of 0.5 and 1.0 M K_2CO_3 solutions. Finally, the autoclave was filled with up to 80% of the total volume, sealed, and maintained at different reaction times and reaction temperatures, respectively. Afterwards, the autoclave was allowed to cool to room temperature naturally. The products were collected and washed several times with acetone, deionized water, and absolute ethanol and then dried in a vacuum oven at 40°C for 4 h.

The surface modification of an iron plate covered with flower-like microstructures was carried out by immersing it in a toluene solution of vinyl triethoxy-silane ($1 \times 10^{-3}\text{ M}$) for 6 h to form a self-assembled monolayer terminated with vinyl groups on the surface. Then the substrate was washed in turn with toluene, chloroform, ethanol, and distilled water and then dried under atmosphere overnight.

Samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) to obtain information on topography, elemental composition, and crystallinity of the textured features formed on the surfaces. The water contact angles (WCAs) on the surfaces were determined using a CA-A contact angle meter (Kyowa Scientific Company, Ltd., Japan) at temperatures of about 20°C and about 45% relative humidity. The static WCAs of each sample were measured five times across the sample surface using the sessile drop method by dispensing $7\ \mu\text{L}$ drops of water on the sample surfaces. A water drop of $5\ \mu\text{L}$ was used for the sliding angle measurement. The water drop was carefully put on the coating and then the substrate was tilted slowly until the drop began to roll.

3 Results and discussion

XRD patterns of flower-like Fe_3O_4 micro/nanoflakes for samples obtained at 180°C for 12 h are shown in Fig. 1a. The diffraction peaks of the samples at $2\theta = 35.42351, 30.08, 62.50, 43.06, 56.89, 18.28, 53.40,$ and 37.10 can be assigned to (311), (220), (440), (400), (511), (111), (422), and (222) planes of Fe_3O_4 , respectively. Except for the reflection located at approximately 44.5° that can be attributed to the iron substrate, all Bragg peaks can be indexed as regular octahedral Fe_3O_4 with lattice constant $a = 8.393\ \text{\AA}$, which is very close to the reported data (JCPDS85-1436, $a = 8.393\ \text{\AA}$). No characteristic peaks of impurities can be detected. The strong and sharp reflection peaks suggest that the as-prepared fractal microcrystals are well crystallized. The diffraction peaks are narrow and strong, indicating the excellent crystallinity. The composition of the product was confirmed by using energy dispersive spectrometry (EDX) analysis. In the EDX spectrum of a typical product (Fig. 1b), the peaks of O and Fe are obviously observed without any other element peaks (the Au peaks in the spectrum are due

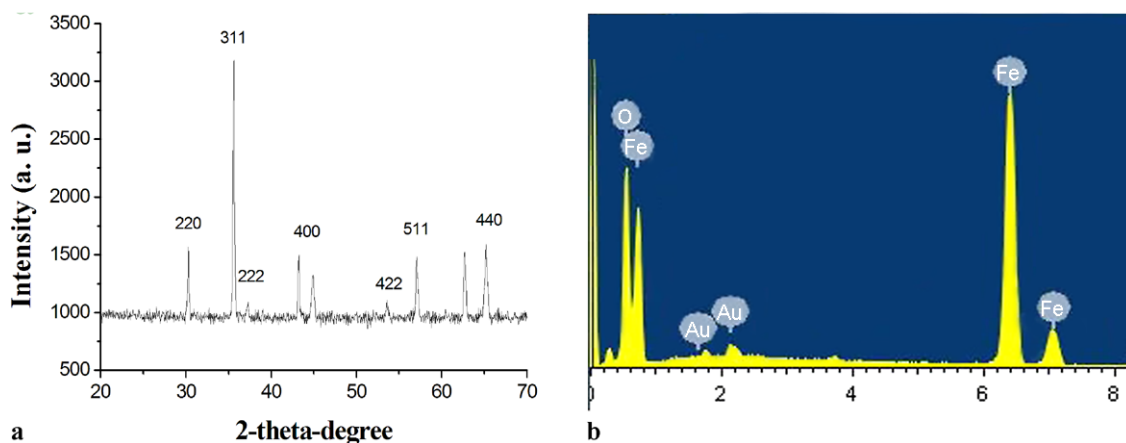
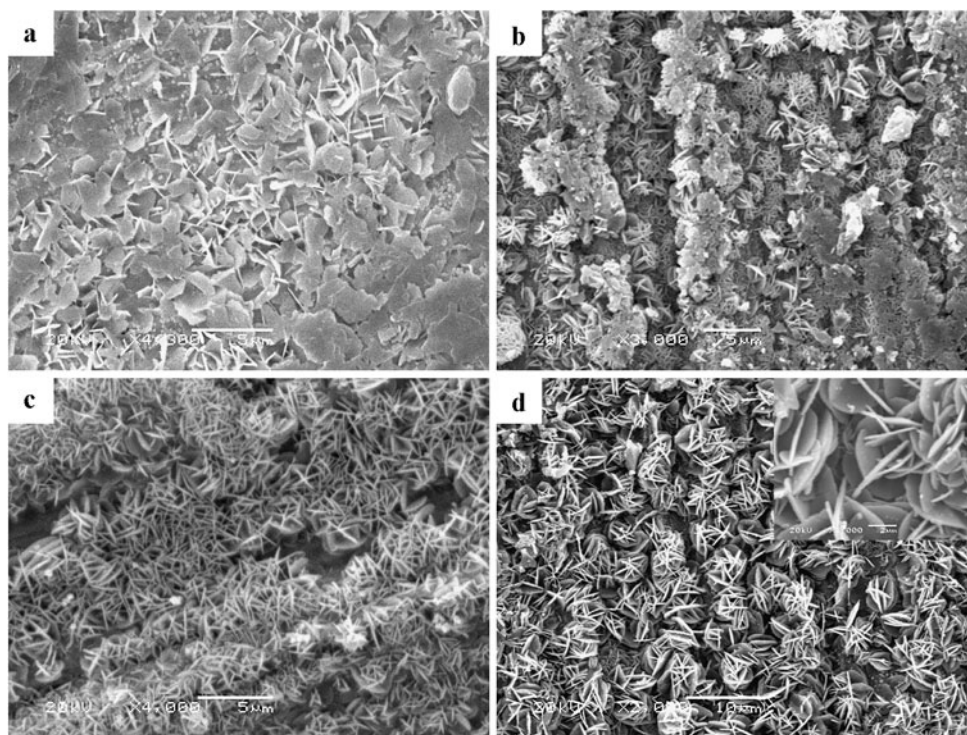


Fig. 1 XRD pattern (a) and EDX spectrum (b) of the sample obtained at 180°C for 12 h

Fig. 2 The representative SEM images of the products prepared at certain reaction conditions for 12 h: (a) 0.5 M K_2CO_3 at 120°C; (b) 1.0 M K_2CO_3 at 120°C; (c) 1.0 M K_2CO_3 at 150°C; (d) 1.0 M K_2CO_3 at 180°C

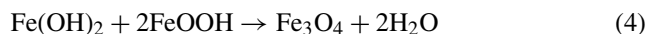
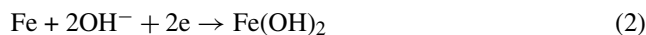
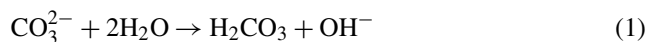


to background from the Au coating), which confirm that the products are iron oxides.

The morphology of the surface microstructure formed on the iron substrate has been observed carefully with SEM. It has been found that the K_2CO_3 concentration and reaction temperature control the size and morphology of the resulting surface. When the K_2CO_3 concentration is 0.5 mol/L, it can be seen from Fig. 2a that a large number of flakes randomly distributed over the iron plate surface are obtained at 120°C for 12 h. However, we do not find flower-like microstructures on the surface. As the K_2CO_3 concentration increases to 1.0 mol/L, some flower-like microstructures have formed on the iron substrate (see Fig. 2b), while those flower-like microstructures partly covered the iron surface. When the reaction temperature reaches 150°C, it can be seen that Fe_3O_4 flakes cover a large area of the iron substrate uniformly and compactly, and most of the flakes are oriented vertically in the upward direction (see Fig. 2c). Two or more flakes were joined with each other forming an interconnected porous structure. No separate or isolated flakes were observed in the overall region of the substrate. As the reaction temperature increases to 180°C, the morphology of the resulting iron plates is similar to that obtained at 150°C. Also, a few of these flakes are oriented upwards with respect to underlying substrate. The diameters of the flower-like microstructures were in the range of 2–6 μm and the enlarged view of a single Fe_3O_4 structure (the inset of Fig. 2d) indicated that the structure exhibited a beautiful flower-like shape, which was termed a ‘microflower’. The microflower was fully grown

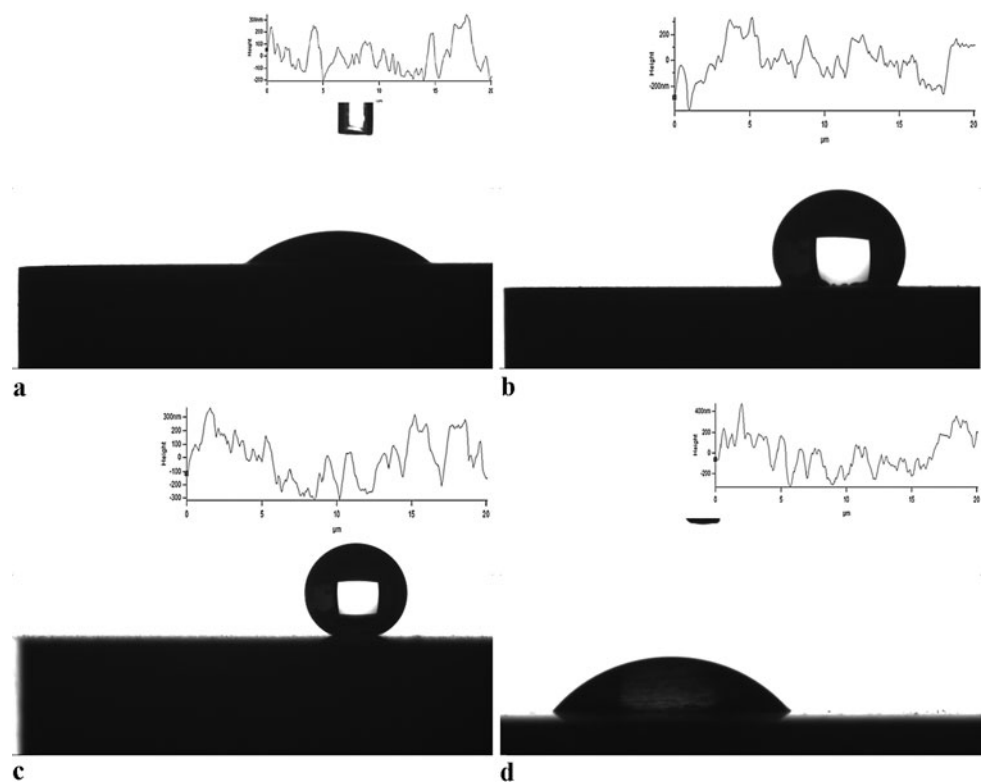
with ‘petals’ 1–3 μm in length and 50–100 nm in width stretching out of the center of the microflower. Such a microstructure was very similar to that of the papillae on natural lotus leaf. The microflowers stacking randomly on the surface made the coating rough in micron scale, while the petals outside the microflowers offered nanoscaled roughness on the surface, leading to the formation of a hierarchical micro/nanoflakes.

The alkalization reaction of ferrous ions has been extensively studied by Cummings and Yan [19, 20] and they proposed a mechanism for the formation of magnetite, Fe_3O_4 . Based on this mechanism, we propose the following route for the formation of Fe_3O_4 :



The formation of octahedral Fe_3O_4 may result from the roles of K_2CO_3 under the appropriate reaction condition. Most probably, OH^- serves as both a ligand and a quasi-surfactant during the reaction. The Fe_3O_4 is formed from the pyrolysis of $Fe^{2+}/Fe^{3+}-OH^-$ first and then is carried by the autogenerated vapor pressure to the low-temperature zone, where it deposits on the iron substrate, nucleates, and self-assembles into networks forming the 3D nanoflowers. In the initial stages, the interplay between the dynamic wetting behavior and the thermally enhanced surface diffusion

Fig. 3 The WAC and the roughness of the surface of an iron plate at different temperatures before (**a, d**) and after (**b, c**) being modified by vinyl tirethoxy-silane: (**a**) 1.0 M K_2CO_3 at 120°C; (**b**) 1.0 M K_2CO_3 at 120°C; (**c**) 1.0 M K_2CO_3 at 180°C; (**d**) 1.0 M K_2CO_3 at 180°C



of Fe_3O_4 adatoms on the substrate may facilitate the formation of the network patterns, rather than forming isolated droplets or a continuous film, at elevated temperature. With increasing reaction temperature, there are more and more OH^- generated by the hydrolysis of CO_3^{2-} to form a basic solution, in which the Fe atoms are easily attacked by the OH^- (as shown in (2)). Thus, the amount of the microflower structures increases with increasing reaction temperature to cover a large area of the iron substrate uniformly and compactly. Although further investigation is necessary to elucidate the mechanism of the growth of the 3D Fe_3O_4 nanoflowers, we believe that the formation of the Fe_3O_4 nanoflowers is initiated along the grain boundaries as these are the most thermodynamically active sites for the precipitation of Fe_3O_4 atoms.

As the surface roughness plays a very important role in the superhydrophobicity, the effects of surface roughness on the wetting properties were studied by comparing the WCAs of the iron surfaces obtained at different reaction temperatures before and after vinyl tirethoxy-silane modifications. When the reaction temperature is 120°C, the temperature was so low that the hydrolysis of CO_3^{2-} is very slow and few flower-like micro/nanostructures were formed on the iron surface. The surface had a low CA of $23 \pm 1^\circ$ and a low roughness of 114.2 nm (Fig. 3a). As the temperature increased to 180°C, the hydrolysis reaction of CO_3^{2-} remarkably occurred and the flower-like structures grow bigger, become continuous, and almost cover the whole plate. The

water CAs and roughness accordingly increased to $37 \pm 2^\circ$ and 147.5 nm (Fig. 3d), respectively. Although the CAs increased from $23 \pm 1^\circ$ to $37 \pm 2^\circ$ due to the increase of surface roughness, they were still far from the superhydrophobicity that was aimed to be obtained. However, after being modified by vinyl tirethoxy-silane, the roughnesses of the surfaces obtained at 120°C and 180°C are up to 155.1 nm and 175.6 nm, respectively. Their contact angles are changed from $124 \pm 1^\circ$ to $157 \pm 1^\circ$ (see Fig. 3b and c), suggesting that the surface changes from hydrophobicity to superhydrophobicity. The much higher WCA of the vinyl tirethoxy-silane modified iron surface obtained at higher reaction temperature compared with the lower WCA of that obtained at lower reaction temperature suggests the importance of high surface roughness in improving the surface hydrophobicity.

The superhydrophobicity of the vinyl tirethoxy-silane modified textured iron surfaces is due to both chemical and topographic factors. As for the former, before vinyl tirethoxy-silane self-assembly, the terminal groups of the oxidized iron surface were O atoms, which are hydrophilic by nature. When the vinyl tirethoxy-silane self-assembly was complete, the hydrophilic O atoms were no longer available and the surface became hydrophobic because of the hydrophobic alkyl chain of the vinyl tirethoxy-silane. As for topography, air was trapped between the textured features, which prevents water droplets from wetting the surface and thus improves the hydrophobicity of the surface. It is reasonable to deduce that the WCA varies according to the surface

roughness of the Fe₃O₄ flower-like structures formed at different reaction temperatures, which indicates that the cooperation of lotus-like micro- and nanohierarchical structures and the hydrophobic alkyl chain of the vinyl triethoxy-silane plays an important role in fabricating the superhydrophobic film.

We also investigated the sliding behavior of a water drop on the as-formed surfaces, which is another important criterion of superhydrophobicity. The surface obtained at 180°C had a SA of $1 \pm 0.2^\circ$. The microstructure of the iron surface and corresponding high WCAs confirmed that we had successfully mimicked the lotus leaf by a simple method. What is more, such superhydrophobicity was obtained just with common metal materials.

4 Conclusions

A superhydrophobic iron surface with high CAs and low SAs was facilely created by a direct in-situ hydrothermal synthesis method. The superhydrophobicity was attributed to the lotus-leaf-like three-dimensional (3D) flower-like micro/nanoflakes with modification with vinyl triethoxy-silane. This method can be extended to other engineering alloy materials to fabricate the superhydrophobic surface through a selection of suitable reactants. The facility and economy of the method make it suitable for the practical application of superhydrophobic surfaces in large area.

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