

Fabrication of Hematite Nanowire Arrays on Pure Iron via Anodization Process for Superhydrophilic Surfaces¹

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Abstract—In this work, hematite nanowire arrays (HNA) were fabricated on pure iron foil by using anodization process in fluoric electrolyte to produce superhydrophilic surfaces. The in situ growth of HNA on iron substrates was ascertained by scanning electron microscopy images, X-ray photoelectron spectroscopy and glancing angle X-ray diffraction measurements. The resultant HNA-bearing iron surfaces showed superhydrophilic property with a contact angle of $7 \pm 2^\circ$, and its super-hydrophilicity remained longer than three days in air.

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1. INTRODUCTION

Anodization process is an effective and promising technique to construct oxide layer on metal surface for anti-corrosion, anti-friction and coloration [1]. In recent years, anodization process has been newly adopted to produce self-organized ordered nanostructure on metallic substrates, and thus attracts more and more attentions in different research fields, such as materials, catalysis, biomaterials and energy fields. Excellent works on fabrication of nanotube arrays on Al and Ti substrates via anodization process have been extensively documented [2, 3]. Other valve metals, such as Zr [4, 5], W [6], Zn [7], Nb [8], Ta [9], have also reported to in situ grow ordered nanostructure on surface by anodization process. However, as a classical object of anodization process, iron (Fe) has not been focused by researchers yet. To the best of our knowledge, only a few studies have reported the fabrication of ordered hematite layers on iron sheet by anodization processes for photocatalytic applications [10, 11]. None of them has ever touched on the other properties, especially surface wettability.

It is well known that surface wettability plays an important role in the adhesion, mass transfer and reaction rate for industrial application of materials, such as metallic packings [12], biomaterials [13] and catalyst [14]. In light of the Wenzel theory [15], the ordered nanostructure of anodized valve metal can dramatically change the surface wettability of metal oxides. Superhydrophilicity of TiO_2 nanotubes array is a typical example due to vertically ordered nanostructure. Iron, frequently used material for metallic packings, has been anodized to form amorphous hematite

layer in alkaline electrolyte for anti-corrosion and coloration applications [1]. It is therefore assumed that the surface wettability of iron would be changed dramatically when anodized hematite layers can be constructed in nano-scale with ordered structure. The superhydrophilic iron surface is potentially significant for industrial and biomedical application.

Herein, the purpose of this study is to fabricate hematite (Fe_2O_3) nanowire array (HNA) on pure iron sheet via anodization process under constant voltage in fluoric electrolyte to give rise to superhydrophilic property. The formation of HNA on anodized iron substrates was characterized by scanning electron microscopy (SEM) images, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction measurements. The surface wettability of anodized iron with HNA was determined by the measurements of water contact angle. The evolution of waster contact angle as a function of time in air was investigated to evaluate the stability of superhydrophilic property of HNA on anodized iron substrates. For comparison purpose, the pristine iron, naturally-oxidized iron, and calcined iron substrates were used as control under same conditions.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Four different types of iron specimens, including pure iron, naturally-oxidized iron, anodized iron, and calcined iron, were prepared. The pure iron sheet was purchased from FuChen Chemical Reagent Factory (Tianjin, China), and was pretreated by mechanical polishing with a series grit of sand paper to obtain a smooth surface. The polished iron sheet was subse-

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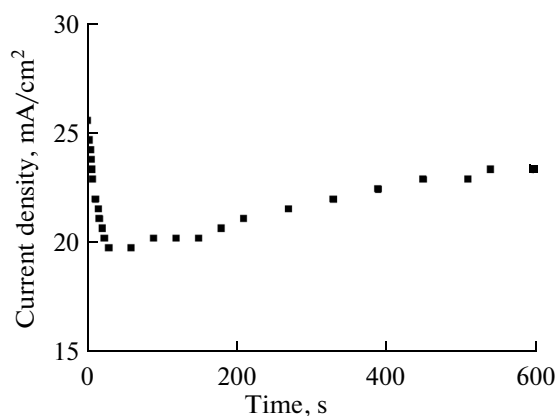


Fig. 1. Current density as a function of time during anodization process in an electrolyte of 0.3 wt% NH_4 + 3 vol % water + EG solution at 40 V.

quently, degraded in acetone by ultrasonic cleaning, and chemical polishing etched in a mixture solution of mix acids: HF, HNO_3 , LA(vol: 2 : 2 : 6). The naturally-oxidized iron was obtained by exposing the pretreated pure iron in air not less than one week for 6 days.

The pretreated iron sheet was anodized in a homemade electrochemical cell with an 300 mL of freshly-prepared electrolyte, which consists of 3 wt% ammonium fluoride in an ethylene glycol solution (3 vol % water in EG). The distance between treated iron sheet, serving as anode, and graphite, serving as cathode, was 8 mm, and the applied potential remained at 40 V. The anodization process was proceeded for 10 min at room temperature. The anodized iron was subsequently annealed in a muffle furnace under atmosphere at 400°C for 2 h. Thus, the anodized iron was obtained. On the contrary, the calcined iron was prepared by directly annealing of pretreated pure iron sheet in the muffle furnace under atmosphere at 400°C for 2 h.

2.2. Water Contact Angle Measurements

The static water contact angles of four different types of iron specimens were measured by a JC2000C1 surface analysis system (Powereach Inc., Shanghai, China) using the sessile drop method with a 3 μL deionized water droplet. After dropping a water droplet onto the sample surface, contact angle can be determined by using the analysis system. The average water contact angle value was obtained by measuring three different locations on the same specimens. The accuracy of contact angle is about $\pm 2^\circ$. To assess the change in surface wettability of HNA anodized iron and calcined iron substrates with exposure time in air, the water contact angles of the two iron specimens were recorded at the predetermined time.

2.3. Surface Characterization

Surface morphology of different iron specimens was characterized by capturing scanning electron microscope (JSM-5900LV, Jeol, Japan) images after the specimens were all sputter-coated with gold/palladium. The surface composition of the anodized iron and calcined iron substrates was determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on a Kratos AXIS XSAM800 spectrometer (Kratos Analytical Ltd., UK) with an Al $K\alpha$ X-ray source (1486.6 eV photons), using procedures described previously. All binding energies (BEs) were referred to the C 1s peak (284.6 eV) arising. The crystal structure of anodized iron was characterized by glancing angle X-ray diffraction (GA-XRD, X'Pert proMPD, the Netherlands) with a Cu- $K\alpha$ 40 kV/40 mA X-ray source (wavelength $\lambda = 0.15406$ nm). The glancing incident was set at 2° and the scanning range was controlled from 30° to 70° at step of 0.02° with 0.5 s per step.

3. RESULTS AND DISCUSSION

Figure 1 shows the current density as a function of time during anodization process in an electrolyte of 0.3 wt% NH_4 + 3 vol% water + EG solution at 40 V. The current density decreases noticeably from 26 mA/cm^2 to 19 mA/cm^2 at initially 60 s, and then gradually increases before leveling off at about 22.6 mA/cm^2 . The result is consistent with the previous observation by Mohapatra et al [16]. The initial decrease in current density is probably associated with the formation of hematite (Fe_2O_3) film on iron sheet, while the subsequent increase in current density is attributed to the diffusion of electrolytic ions through the porous layer. When the equilibrium between hematite formation and electrolytic ion diffusion is established, the current density becomes constant. Thus, the hematite nanotube arrays (HNA) are successfully generated on the pristine iron substrates.

Figure 2 shows the representative SEM images and the corresponding water contact angle profiles of different iron substrate surfaces. The pristine pure iron specimens show a relatively uniform and smooth surface, albeit with the presence of some scratches introduced during polishing (Fig. 2a). The static water contact angle on the pristine pure iron is about $50 \pm 2^\circ$ (Inset of Fig. 2a). The dense and porous oxide layers are readily observed on the naturally-oxidized iron surface (Fig. 2b), accompanying with the water contact angle of around $85 \pm 2^\circ$ (Inset of Fig. 2b). Well-defined vertical nanowire arrays are intensively distributed over the entire surface of the anodized iron specimens (Fig. 2c), and thus leading to the sharp decrease in water contact angle to approximately $7 \pm 2^\circ$ (Inset of Fig. 2c). On the basis of the Wenzel theory [15], $\cos \theta = r \cos \theta^*$, the ordered nanowire-structures play a significant role in improving the wetting behavior of hematite layers, as the roughness factor, r , of iron surface is substantially

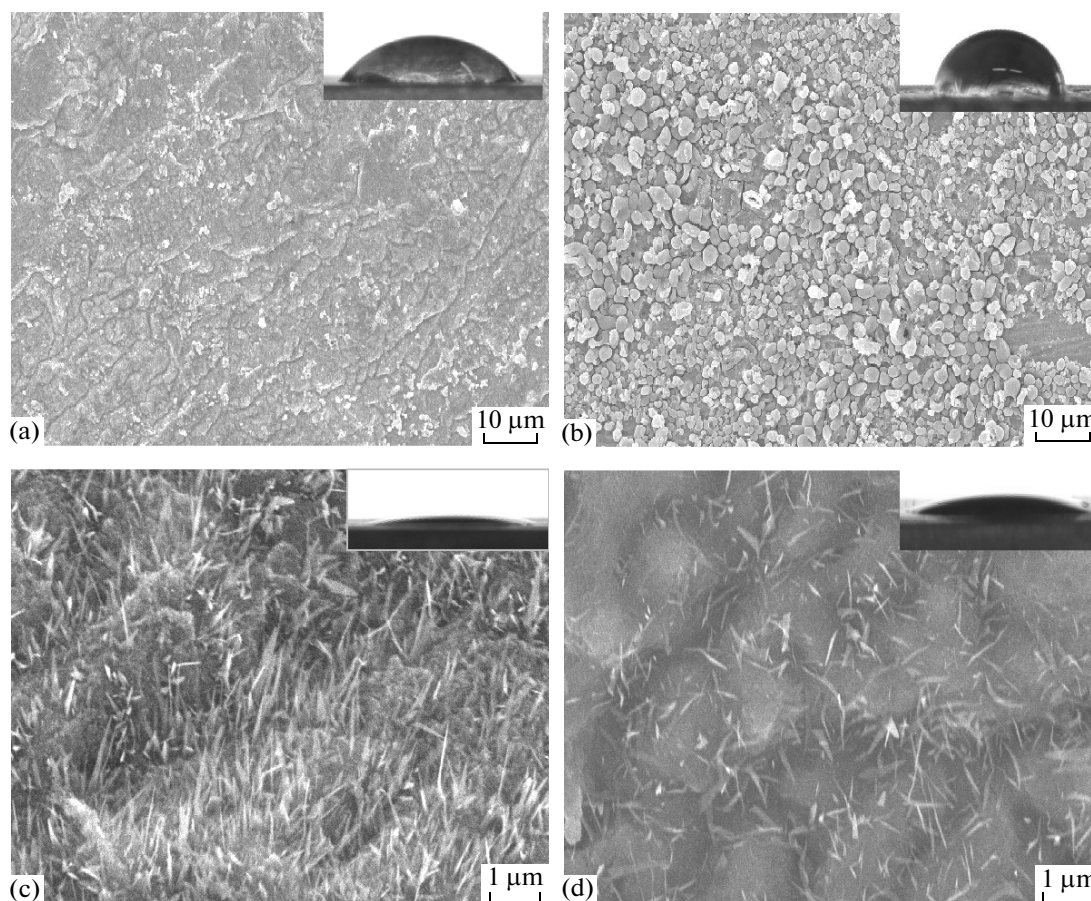


Fig. 2. Representative SEM images of different iron substrates: (a) pristine iron, (b) naturally-oxidized iron, (c) anodized iron with nanowire arrays, (d) calcined iron. The insets are the contact angle profiles of water droplet on the corresponding iron substrates.

augmented after anodized. As for the calcined iron specimens, the nanowire is also visible, but sparse and randomly (Fig. 2d), on the surface, together with its water contact angle as low as about $10 \pm 2^\circ$ (inset of Fig. 2d), attributable to the nanostructure on the substrate surface as well. The superhydrophilic property was thus conferred on the anodized and calcined iron substrates.

GAXRD measurement was conducted to determine the crystal structure of the nanowires on the iron substrates. Figure 3 shows the XRD peak patterns of the anodized iron and calcined iron samples. The appearance of predominately (104) and (110) diffraction peaks confirms the formation of hematite peaks on both iron samples, although the anodized iron shows stronger signals, indicative of better crystallization (Fig. 3a). The result is in good agreement with the presence of dense hematite nanowire arrays on the anodized iron surfaces. The other peaks correspond to magnetite and iron, respectively. The hematite nanowire arrays are therefore ascertained to grow from the iron substrates.

X-ray photoelectron spectroscopy in Fig. 4 reveals the chemical components at surface of (Fig. 4a) anodized and (Fig. 4d) calcined iron samples. Three ele-

ments, Fe, O and C, can be affirmed and no others are found. And the residual carbon could be the contamination in XPS testing.

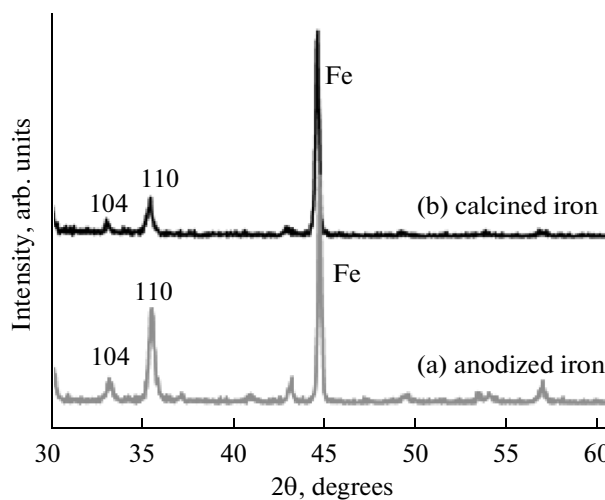


Fig. 3. X-ray diffraction pattern of the anodized iron with nanowire arrays and calcined iron substrates.

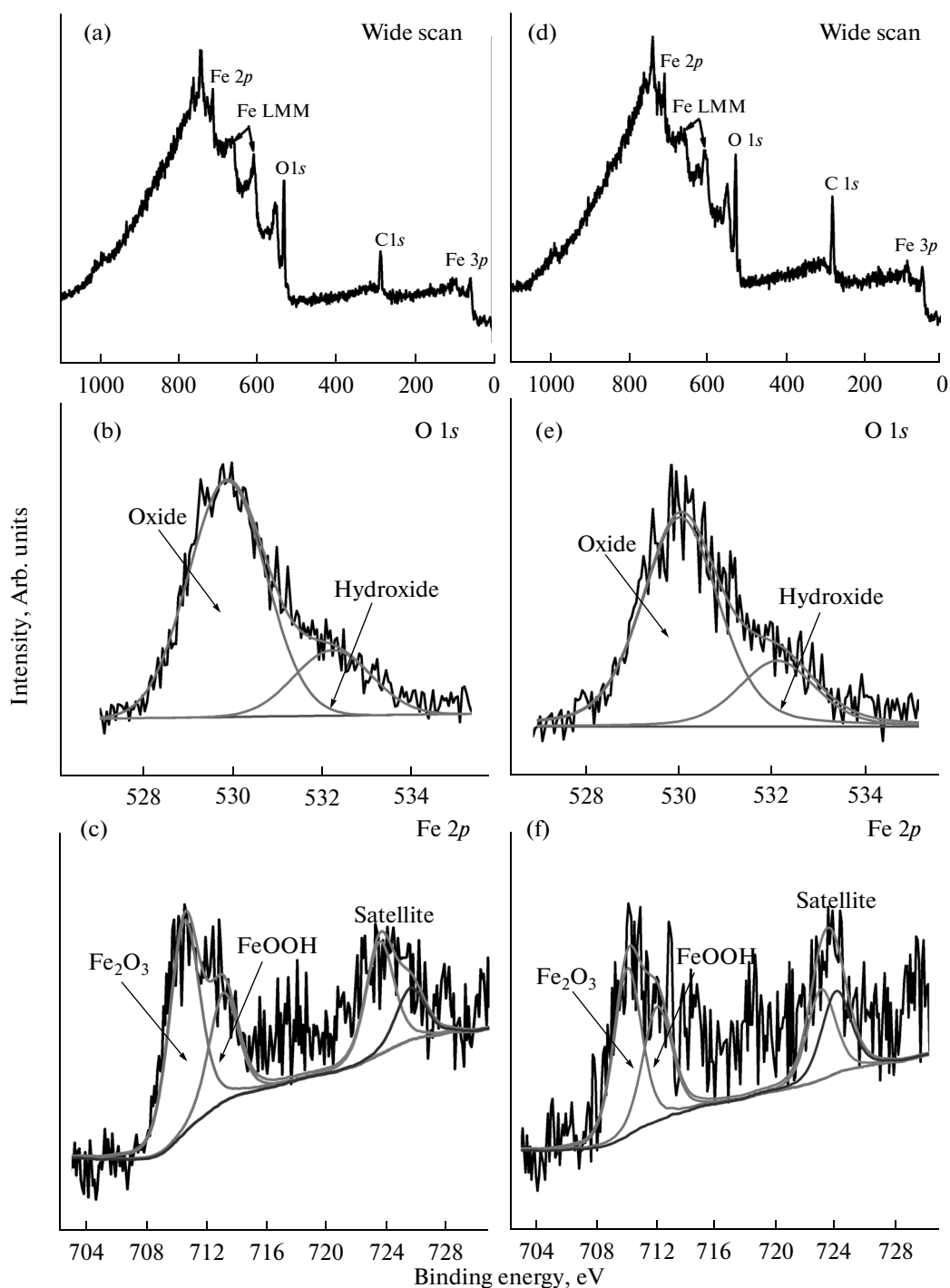


Fig. 4. Wide scan, Fe $2p$ and O $1s$ core-level XPS spectra of (a, b, c) anodized iron with nanowire arrays and (d, e, f) calcined iron substrates.

High-resolution spectra of the Fe $2p$ and O $1s$ were acquired to better understand the differences in the chemical composition of the surface on anodized (Fig. 4b, 4c) and calcined (Fig. 4e, 4f) iron samples. The spectrum of Fe $2p_{3/2}$ from anodized surface is shown in Fig. 4c. It can be curve-fitted with two peaks at binding energies of 711.2 eV and 713 eV, corresponding to Fe₂O₃ and FeOOH respectively. And from the Fig. 4f, the

spectrum also indicates the existence of two peaks with binding energies of 711.3 eV and 712.2 eV, attributable to Fe₂O₃ and FeOOH respectively. This result excludes the other possibilities of super-hydrophobicity of HNA.

To evaluate the stability of superhydrophilicity of anodized and calcined iron specimens, the changes in water contact angles as a function of exposure time in air were recorded, and are shown in Fig. 5. As shown

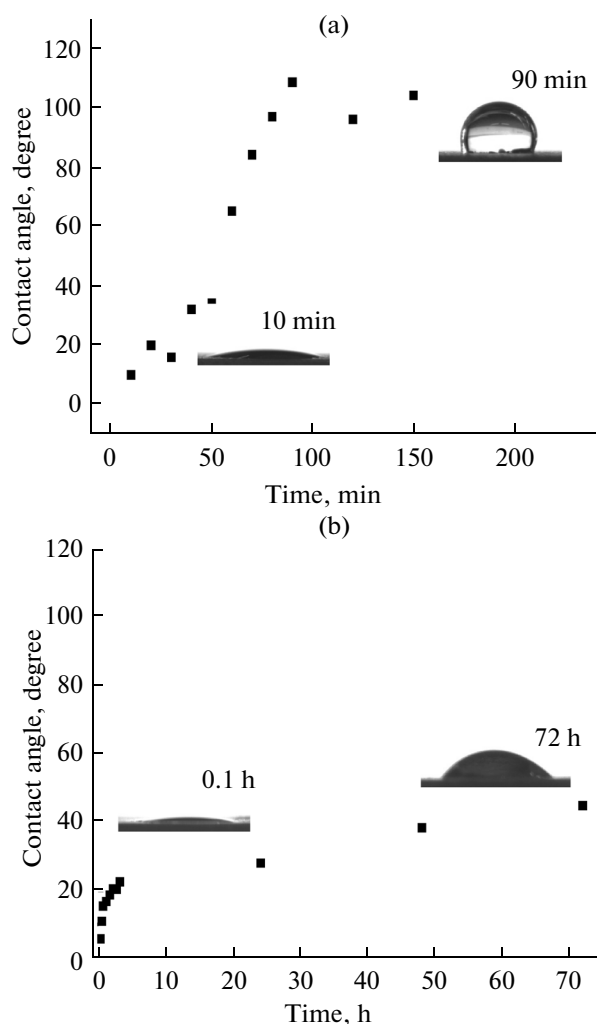


Fig. 5. The changes in water droplet contact angle of as a function of time in air for the (a) calcined iron and (b) anodized iron with nanowire arrays. The insets are the corresponding water contact angles after a specific time in air.

in Fig. 5a, the contact angles of the calcined iron specimens increase rapidly from about $10^\circ \pm 2^\circ$ to about $105^\circ \pm 2^\circ$ after 90 min of exposure in air (Fig. 5a). On the contrary, the contact angle of anodized iron increases slowly from about $7^\circ \pm 2^\circ$ to about $45^\circ \pm 2^\circ$ after 72 h (Fig. 5b), indicating that the hydrophilic property of anodized iron sample is more stable than that of the calcined iron specimens. This phenomenon is probably associated with the different nanostructures of the two iron specimens. To further confirm this point, SEM images of the anodized iron and calcined iron samples after 6 days of exposure in air were captured, as shown in Fig. 6. Obviously, the typical hematite nanowires were still visible on the surface of anodized samples (Fig. 6a), although the density of nanowires is substantially reduced. On the contrary, no nanowires can be detected on the surface of cal-

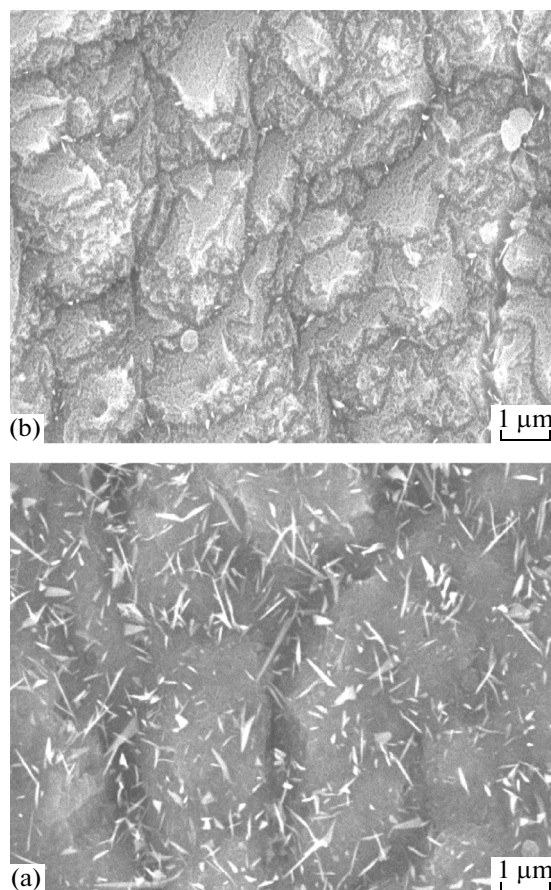


Fig. 6. Representative SEM images of (a) anodized iron with nanowire arrays, and (b) calcined iron after exposed in air for six days.

cined iron specimens, and the surface become coarse and porous (Fig. 6b), which is probably attributable to the recrystallization of hematite. This result confirms that the HNA layers are the key factor to super-hydrophobicity of anodized iron substrates, and the vertical ordered nanostructure and density of HNA play an important role in the persistence of surface super-hydrophilicity.

4. CONCLUSIONS

In this work, the ordered hematite nanowire arrays (HNA) were successfully fabricated on the pure iron by using simple electrochemical anodization process. The resultant HNA-bearing iron surface exhibited superhydrophilic property with a water contact angle of about $7^\circ \pm 2^\circ$. This phenomenon was attributed to the highly ordered nanostructure of HNA on the anodized iron surface, as revealed by SEM images and GAXRD spectra. The stability and persistence of superhydrophilic was found to be dependent on the density of HNA on the iron surfaces.

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