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# Facile synthesis of hematite nanoplates and their self-assembly generated by domain growth of NaCl

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ABSTRACT

Hematite nanoplates with exposed (0 0 1) facets were fabricated through a solvothermal process using $FeCl_3$ and $CH_3COONa$ in an ethanol solution because of $CH_3COO^-$ groups ascribed on the (0 0 1) facets of $Fe_2O_3$. Hexagonal-like nanoplates, octahedron, and nanoplates were created through adjusting the amount of $CH_3COONa$. Solvents were crucial for the preparation of the nanoplates because irregular $Fe_2O_3$ particles rather than nanoplates were created once isopropanol or the mixture of water and ethanol instead of ethanol. The growth process of $Fe_2O_3$ with various morphologies was discussed. Additionally, we observed the self-assembly of the nanoplates into one- or three-dimensional dendritic morphology through a droplet dewetting technique by using NaCl molecules as scaffolds. This phenomenon is ascribed to the domain growth of NaCl to form fractal shapes and a hydrodynamic mechanism through outward capillary flow. The morphologies of the assemblies are related to the evaporation speed of solvent during droplet dewetting.



## 1. Introduction

Hematite ($\alpha$-$Fe_2O_3$), an *n*-type semiconductor ($E_g \sim 2.1$ eV), is a stable and useful material due to its superior physicochemical properties, low processing cost and high resistance to corrosion, and has wide commercial and industrial applications in various fields, such as magnetic devices, catalysts, gas-sensing, pigments and rechargeable lithium-ion batteries as well as in other biological and medical fields [1–3]. The size, shape, and surface situation of nanomaterials tremendously alter their physical and chemical properties. Typical nanostructures including nanoparticles, nanorods, nanoribbons, nanoplates, nanowires, nanotubes, and nanoprisms are promising in application areas such as chemical and biological sensors, transistors, separations, catalysts, and lasers [4–6]. For example, Yu et al., reported that unusual $\alpha$-$Fe_2O_3$ cage-like superstructure hollow spheres with high specific surface areas, and small crystallite size promotes its photocatalytic activity for rhodamine B in the presence of hydrogen peroxide [7]. Wang et al. demonstrated that the as-prepared porous $Fe_2O_3$ nanorod would be an ideal candidate for application in ethanol sensors [8]. Zheng group reported that 3 dimensional (3D) $\alpha$-$Fe_2O_3$ nanoflowers with porous structure show excellent electrochemical, magnetic, and photocatalytic properties [9].

Compared with 1D and 3D nanostructures, the synthesis of 2D nanoplates has not been well investigated yet. Very few reports have addressed the formation of the nanoplates nanostructures. 2D nanostructures can be obtained through the limitation of the oriented growth using the capping molecule. Liu and co-workers have obtained a complex hexagonal ZnO nanostructure with capping of the citric acid using a seed growth procedure, which adsorbs preferably on the (0 0 1) surface of ZnO and slows down the crystal growth along the *c*-axis [10]. Wu group has synthetized hexagonal oxide or hydroxide using capping molecule of citric acid, which inhibits crystal growth along the (0 0 1) direction due to its chelating effect [11]. Chen et al. have synthesized nanodiscs using citric acid as a capping agent which allows the etching to proceed favorably along one particular direction [12].

In recent years, the synthesis of complex architectures assembled using nanoparticles, nanorods, nanoplates, nanosheets, nanotubes as building blocks has drawn a lot of interest due to the potential applications of complex architectures in electronic, magnetic, optoelectronic, catalytic, and biomedical fields. Zhu's group has synthesized 3D porous flower-like hierarchical nanostructures of $\alpha$-$Fe_2O_3$ without employing templates or matrices, which were composed of 2D nanopetals though the intercrossed with each other and constructed from nanobricks [13]. Ma et al.

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**Table 1**
Preparation conditions of $Fe_2O_3$ samples

| Sample | $FeCl_3·6H_2O$ (g) | $NaAC·3H_2O$ (g) | PVP (g) | Ethanol (mL) | Water (mL) | Isopropanol (mL) | Temperature (°C) | Time (h) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.676 | 0.728 | N/A | 25 | N/A | N/A | 200 | 16 |
| 2 | 0.676 | 1.092 | N/A | 25 | N/A | N/A | 200 | 16 |
| 3 | 0.676 | 1.457 | N/A | 25 | N/A | N/A | 200 | 16 |
| 4 | 0.676 | 2.914 | N/A | 25 | N/A | N/A | 200 | 16 |
| 5 | 0.676 | 4.371 | N/A | 25 | N/A | N/A | 200 | 16 |
| 6 | 0.676 | 1.457 | N/A | 12.5 | 12.5 | N/A | 200 | 16 |
| 7 | 0.676 | 1.457 | N/A | N/A | N/A | 25 | 200 | 16 |
| 8 | 0.676 | 1.457 | 0.1 | 25 | N/A | N/A | 200 | 16 |
| 9 | 0.676 | 0.728 | 0.1 | 25 | N/A | N/A | 200 | 16 |

reported that porous plate-like $Fe_2O_3$ mesocrystals, composed of single crystalline nanoparticles, were prepared via a controlled solvent evaporation process in the presence of an ionic liquid [Bmim]Cl [14]. However, it is still desired to directly fabricate 2D nanomaterials because of the limitation application of the complex architectures consisted of small nano-units.

Single-crystalline $Fe_2O_3$ nano- and micro-particles with controlled shapes and phases are prepared using aero-sol-assisted molten salt syntheses [15] or hydrothermal/solvothermal method [16]. Especially, hydrothermal/solvothermal has become one of the most popular methods to get inorganic nanostructured materials, especially metals and their oxides because of higher pressure and higher temperature occurred in this method and can increase the solubility of solids and accelerate reactions between solid species. In this Article, an effective route for the synthesizing of monodispersed $\alpha$-$Fe_2O_3$ nanoplates without employing templates has been developed by controlling the reaction conditions. The morphology and sizes of resulting samples were investigated in detail. The effects of experimental conditions such as reaction time and the amount of precursors on the morphology and size of the sample were studied systematically. As a result, $\alpha$-$Fe_2O_3$ samples revealed nanoplate, hexagonal-like nanoplate, and octahedron morphologies. The formation mechanism was discussed in detail. In addition, the nanoplates were assembled into micro spheres and arrange into a line along (0 0 1) direction in a face-to-face situation by the domain growth of NaCl. In contrast, the assembly was not observed in the case of the nanoplates prepared using polyvinylpyrrolidone (PVP).

## 2. Experimental

### 2.1. Materials

$FeCl_3·6H_2O$, PVP ($M_w \sim 40{,}000$), $CH_3COONa·3H_2O$ (NaAC), isopropanol, and ethanol were purchased from China National Pharmaceutical Group Corporation (Sinopharm). Deionized water used for all experiments was supplied by a Millipore system (18.2 $M\Omega\,cm^{-1}$). All chemicals were used as received without further purification.

### 2.2. Synthesis of $\alpha$-$Fe_2O_3$ samples

The $\alpha$-$Fe_2O_3$ samples were synthesized by a solvothermal process in ethanol. In a typical synthesis of $\alpha$-$Fe_2O_3$ samples, 0.676 g of $FeCl_3·7H_2O$ and 1.457 g of $NaAC·3H_2O$ were dissolved in 25 mL ethanol wit stirring. Then, the solution was added into a Teflon-lined stainless-steel autoclave sealed for heat-treatment at 200 °C for 16 h. After reaction, the autoclave was cooled down to room temperature. The red samples were collected and washed with ethanol and water for several times, and then dried at 80 °C for 6 h in air atmosphere. To investigate the influence of experimental conditions on the size and morphology of samples, experimental parameters were adjusted. The detail of experimental data is listed in Table 1.

### 2.3. Characterization

The transmission electron microscopy (TEM) observation was carried out using JEM-100CX and H-800 transmission electron microscopes. The X-ray diffraction (XRD) patterns of samples were recorded by X-ray diffractometer using a Bruker D8 Advance with a Cu Kα source (0.154 nm) in a $2\theta$ range of 15–70° with a scan step of 0.02°/min. The morphology observation of samples was taken on a field emission scanning electron microscopy (SEM, QUANTA 250 FEG, FEI, America). The Fourier-transform infrared (FTIR) spectroscopy of samples was taken using a Nicolet 380 instrument in a 500–4000 $cm^{-1}$ range. Samples were dispersed in hexane and then dropped on a KBr disk to evaporate ethanol.

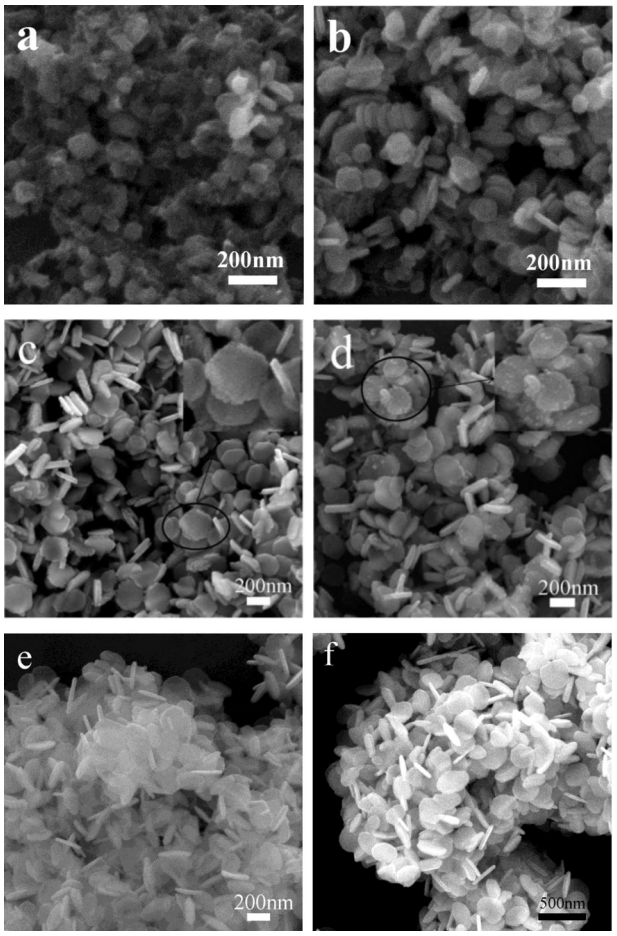


**Fig. 1.** SEM images of $Fe_2O_3$ nanoplates (sample 3 as shown in Table 1) prepared using different time. (a), 2 h (b), 4 h (c), 6 h (d), 9 h (e), 16, (f), 20. Insets in (c) and (d) show the images with a high magnification.