



## Full Length Article

## Facet-controlled synthesis of polyhedral hematite/carbon composites with enhanced photoactivity



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## ABSTRACT

Much effort has been made to develop the semiconductor photocatalysis, but it is still challenging to fabricate low-cost and high-activity photocatalysts. In this study, Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) with three kinds of morphologies including dodecahedron, tetrakaidecahedron and hexagonal nanoplates have been synthesized without any organic reagents. The photocatalytic performance reveals that the dodecahedron with exposed  $\{1\ 0\ 1\}$  facets is superior to the hexagonal nanoplates with predominant exposure of  $\{0\ 0\ 1\}$  facets in the case of similar BET surface area. For further enhancement of photocatalytic activity, carbon layer was coated on dodecahedral  $\alpha\text{-Fe}_2\text{O}_3$  through the self-polymerization of dopamine and following pyrolysis at 400 °C under Ar flow. Compared with the pristine dodecahedral  $\alpha\text{-Fe}_2\text{O}_3$ , the  $\alpha\text{-Fe}_2\text{O}_3/\text{C}$  composites exhibit stronger visible absorption, lower photoexcited electron-hole pairs recombination rate and better photodegradation activity. The photocatalytic performance showed the degradation rate of  $\alpha\text{-Fe}_2\text{O}_3\text{-D}/4.5\text{C}$  is nearly 6 times higher than pristine  $\alpha\text{-Fe}_2\text{O}_3$ , which have great potential for photocatalysis applications.

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## 1. Introduction

As a n-type semiconductor, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) possesses a favorable bandgap energy of 1.9–2.2 eV, and has been extended a wide range of applications such as sensors [1], solar cells [2], lithium ion batteries [3,4], and photocatalysis [5], field emitters [6], pigments [7], PEC water splitting [8–10] because of its non-poisonous, chemical stability and low cost. Generally, the chemical and physical properties of crystals will be largely relevant to the surface morphology which emerges diverse surface atoms arrangement and electron structure [11]. Meanwhile, the size and shape of crystal has been precisely tailored on account of the rapid development in material science in recent years [12]. Thus, innumerable study efforts have been dedicated on the controllable synthesis of micro- and nanocrystals of  $\alpha\text{-Fe}_2\text{O}_3$  with various geometries and exposed index facets. For instance, Zhou et al. fabricated 1D nanorods, 2D nanoplates, and 3D nanocubes as model photocatalysts and the reactivity sequence of exposed facets can be rationalized as  $\{1\ 1\ 0\} > \{0\ 1\ 2\} > \{0\ 0\ 1\}$  [13]. Zhao et al. synthesized two kinds of homogeneous  $\alpha\text{-Fe}_2\text{O}_3$  nanocrystals, rhombohedral  $\alpha\text{-Fe}_2\text{O}_3$  nanocrystals with exposed  $\{1\ 0\ 0\}$  and  $\{0\ 0\ 1\}$  facets, truncated-dodecahedral nanocrystals with a predominant  $\{1\ 1\ 0\}$  facet, and demonstrated the activity of  $\{1\ 1\ 0\}$  was superior than

$\{1\ 0\ 0\}$  and  $\{0\ 0\ 1\}$  [14]. Furthermore, oblique and truncated nanocubes with exposure of  $\{0\ 1\ 2\}$  and  $\{1\ 0\ 4\}$  dominant facets were synthesized in the presence of oleylamine, acetylacetone and oleic acid, and testified that the photocatalytic performance of  $\{0\ 1\ 2\}$  facets was active than  $\{0\ 1\ 2\}$  facets [15]. Yin et al. fabricated two uniform  $\alpha\text{-Fe}_2\text{O}_3$  nanocrystals: tetrakaidecahedra with  $\{0\ 1\ 2\}$ ,  $\{1\ 0\ 2\}$ ,  $\{0\ 0\ 1\}$ , and oblique parallelepipeds with  $\{0\ 1\ 2\}$ ,  $\{0\ 1\ 4\}$ ,  $\{2\ 1\ 0\}$  high-index facets, also concluded the photodegradation rate of tetrakaidecahedra which had more high-index facets was superior to oblique parallelepipeds [16]. However, these methods all suffer from the follow weaknesses: (1) the use of organic reagents, (2) the process is complicated to control. Despite these efforts that researchers have made, it still encounters numerous obstacles of poor absorption-coefficient, low electrical conductivity and fast electron-hole pairs recombination.

Carbon materials, which include graphene, carbon nanotube, carbon sphere, amorphous carbon et al., exhibit favourable electrical conductivity [17], excellent electrochemical properties [18] and intense light absorption in the visible region. Graphene, however, suffers from severe aggregation as recombination with other materials. Meanwhile, the carbon nanotube and carbon sphere are difficult to coat for the formation of core-shell structure. On the contrary, amorphous carbon is a potential and unique coating material for hybrid structures, and it can be obtained by inexpensive and environmentally benign processes. Lou et al. have firstly evidenced that a carbon coated CdS nanohybrid exhibits signifi-

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cantly enhanced photostability and photocatalytic ability, indicating that thin carbon layers with a degree of graphitization can facilitate electron transfer and prevent the active core materials from contacting with oxygen and moisture in the air [19]. More importantly, the properties of the final photocatalyst might also be modified, such as optical properties, and the absorption capacity, by modification of the carbon nanocoating [20].

Herein, three kinds of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals with different morphologies and index facets were synthesized by simply adjusting the concentration of OH<sup>-</sup>: dodecahedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles with 12 exposed {1 0 1} facets, tetrakaidecahedral particles with 12 exposed {1 0 1} facets and 2 {0 0 1} facets, and hexagonal nanoplates with 2 predominant {0 0 1} facets. It was found that the dodecahedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals with more high-index facets revealed the most remarkable photodegradation activity for Rhodamine B, and the hexagonal nanoplates  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> displayed the inferior photodegradation activity. For further improving the photocatalytic property of dodecahedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the carbon layer was coating by budget and environmentally benign methods at room-temperature, simply using dopamine as a precursor, and the thickness is convenient to adjust by changing the reaction time. According to the photodegradation study, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/C composites showed a superior photocatalytic activity than pristine octodecahedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> because of the stronger visible absorption and effective electron transfer, which is evidenced by PL and UV-vis spectroscopy.

## 2. Experimental

### 2.1. Fabrication of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> polyhedron

In a typical experiment, a given amount solution of 1 M NaOH (Sinopharm Chemical Reagent Corp.,  $\geq 99\%$ ) was dropwise added into the 60 ml of H<sub>2</sub>O solution of FeCl<sub>2</sub>·4H<sub>2</sub>O (Sinopharm Chemical Reagent Corp.,  $\geq 99\%$ ) in a slow rate of 4 ml h<sup>-1</sup> to induce the precipitation reaction under vigorous stirring. After that, the resultant mixture was transferred into a Teflon-lined autoclave, and heated at 160 °C for 10 h. Following natural cooling to room temperature, the solid production was collected by centrifugation at 12,000 rpm for 3 min and washed with deionized water and ethanol for three times, respectively. The production was then dried in the oven at 60 °C for 6 h and further treated at 300 °C for 2 h in air with a rate of 2 °C·min<sup>-1</sup> to obtain the final  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> polyhedron.

### 2.2. Fabrication of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@C core-shell nanocomposites

For different thickness coating of carbon layer, 0.1 g obtained  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-D was dispersed in the solution of dopamine hydrochloride (3 mg·mL<sup>-1</sup>) buffered at pH 8.5 and stirred for different times (0.5 h, 1 h, 2 h). After coating, the sample was collected and dried in the oven at 60 °C for 8 h and further treated at 400 °C for 2 h in a tube furnace under Ar flow.

### 2.3. Characterization

The wide-angle XRD patterns were carried out on a Bruker D8 advance powder diffractometer using Cu K $\alpha$ 1 radiation (1.5405 Å). Scanning electron microscopy (SEM) was performed with a FEI Quanta 450 field emission scanning electron microscope. TEM images were obtained using a Tecnai G2 F30 transmission electron microscope at an acceleration voltage of 300 kV. N<sub>2</sub> adsorption-desorption isotherms were gained on a Micromeritics Tristar 3020 at -196 °C under continuous adsorption conditions. Brunauer-Emmett-Tellwe (BET) and Barrett-Joyner Halenda (BJH) methods were used to estimate the surface area, the pore size dis-

tribution and the pore volume. Photoluminescence (PL) spectra were carried out at room temperature on a fluorescence spectrophotometer (RF-5307) with an excitation wavelength of 300 nm. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples was carried out using a Shimadzu UV-3600 PC ultraviolet visible near-infrared spectrophotometer. X-ray photoelectron spectroscopy (XPS) were measured with an ESCALAB 250 X-ray photoelectron spectrometer using Al K $\alpha$  ( $h\nu = 1486.6$  eV) radiation. Raman spectra were collected by using Raman Microscopy (Horiba, LabRAM HR Evolution, France) with an excitation wavelength of 532 nm.

### 2.4. Photocatalytic performance

The degradation of Rhodamine B was conducted under mercy lamp (300 W) radiation. Typically, 10 mg of photocatalysts were ultrasonic dispersed in the solution of RhB (10 mg/L) with additional 0.7 ml H<sub>2</sub>O<sub>2</sub> ( $\geq 30$  wt%). Before the degradation, there would be an adsorption-desorption equilibrium process about 40 min in the dark. After being exposed to the light, the suspension (3 ml) was taken away, centrifuged and analyzed at a UV-Vis spectrophotometer at 550 nm.

## 3. Results and discussion

### 3.1. Structure and morphology analysis

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals with different facets were synthesized by a simple hydrothermal process using NaOH as precipitant for Fe<sup>3+</sup> ions. The morphologies and structure were investigated by the scanning electron microscopy (SEM), as shown in Fig. 1. Fig. 1a-c show the representative morphology transition of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> from dodecahedron, tetrakaidecahedron to the hexagonal nanoplates with different addition amount of NaOH solution (a for 2 ml, b for 5 ml, c for 15 ml, which named as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-D,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-T,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-H, respectively). The dodecahedron  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is consisted of 12 {1 0 1} high-index facets, the tetrakaidecahedron is consisted of 12 {1 0 1} high-index facets and 2 {0 0 1} low-index facets, and the hexagonal nanoplates is predominantly consisted of 2 {0 0 1} low-index facets. By regulating the concentration of OH<sup>-</sup>, the {0 0 1} facets have emerged and the ratio increases with the increasing of OH<sup>-</sup>, meanwhile the shapes have been compressed from up to bottom. It is clearly observed that the size of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles has increased from a rim size about 300 nm–500 nm, and to 1.8  $\mu$ m. The X-ray diffraction (XRD) pattern of the obtained polyhedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is showed in Fig. 1d. It is evident that all of the expected peaks can be indexed to the hexagonal structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS card No.99-0060) with structure parameters of  $a = b = 5.036$  Å,  $c = 13.747$  Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ , which means no impurities have been found in the as-prepared products. The diffraction peaks of  $2\theta$  values at 24.1°, 33.2°, 35.6°, 40.9°, 49.5°, 54.1°, 57.6°, 62.4°, 64.0°, 72.0°, 75.5° can be corresponded to (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (0 1 8), (2 1 4), (3 0 0), and (1 0 1 0) crystal planes of hexagonal iron oxide, respectively.

The simple illustrations for the morphological transformation from the dodecahedron to hexagonal nanoplates with the increasing amount of NaOH are depicted in Scheme 1. Generally, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts were prepared by slowly dropping NaOH into Fe<sup>2+</sup> solution under vigorous stirring [21], which could conduct the formation of dark green precipitate of Fe(OH)<sub>2</sub>. Quickly, the Fe(OH)<sub>2</sub> will be oxidized to Fe(OH)<sub>3</sub> and the precipitate transforms into red brown. When hydrothermal reaction prolonged to 10 h or longer, the Fe(OH)<sub>3</sub> would decompose to form the stable  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. The formation process of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be described as follows:

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