



Phase transformation-induced crystal plane effect of iron oxide micropine dendrites on gaseous toluene photocatalytic oxidation



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ABSTRACT

Hematite (α -Fe₂O₃), magnetite (Fe₃O₄), and maghemite (γ -Fe₂O₃) micropine dendrites were synthesized by a facile hydrothermal method and oxidation-reduction process. The samples have been thoroughly characterized by various physicochemical techniques. The adsorption ability, quantum efficiency, and the photo-induced charge separation of the electron-hole pair in the samples were demonstrated by the XPS, FTIR, UV-vis, and PL spectroscopy. The α -Fe₂O₃ showed higher catalytic activity than the other two samples for photocatalytic oxidation of gaseous toluene. This may be attributed to the phase transformation-induced crystal plane effect of the α -Fe₂O₃ micropine dendrite, which has relatively more reactive crystal planes {001} and {110} exposed on the surface of α -Fe₂O₃.

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1. Introduction

Fe₂O₃ nanomaterials have attracted increasing attention because of their inherent energy and environmental benign character in practical applications such as catalysis, lithium ion battery, magnetic storage, and gas sensors [1,2]. To date, four crystal-phase structures, α -, β -, γ -, and ε -Fe₂O₃, have been discovered. Among them, β - and ε -Fe₂O₃ have been rarely studied due to their poor thermal stabilities under reaction conditions. Until now, highly crystalline α - and γ -Fe₂O₃ are the most interesting and potentially useful phases. α -Fe₂O₃ has been used in heterogeneous catalysis, magnetic materials, and many other fields. γ -Fe₂O₃ is traditionally used in the magnetic recording industry. In order to promote their performances, substantial efforts have been made in fabricating nanocrystalline Fe₂O₃ with tailored crystal-phase, size, and morphology. Several previous reviews have well summarized the important progresses on the synthesis and applications of iron oxides, including polymorphous transformations [3], shape and size control [4], superparamagnetic and heterogeneous catalytic properties of iron oxides [5,6].

It is well understood that the catalytic properties depend on the morphology, particle size, and specific surface area. In the past, Fe₂O₃ nanocrystals with various morphologies such as OD

(particles, cubes) [7], 1D (rods, wires, tubes, and belts) [8], 2D (disks, films) [9], 3D (dendrites, flowers, and spheres) [10], and hybrids, have been synthesized by different methods, and their various functions have been tested. However, up to now, very limited literature is available on the photocatalytic study of dendritic Fe₂O₃ particles. Wang et al. once synthesized α -Fe₂O₃ micropine dendrites, snowflakes, and bundles by tuning the total concentration of the two iron precursors K₄[Fe(CN)₆] and K₃[Fe(CN)₆], and discovered that they were active photocatalysts for degradation of salicylic acid [11]. Li et al. have recently compared the photocatalytic toluene oxidation activity of hollow spindle-like α -Fe₂O₃ with the Ag-loaded one [12]. Herein, we selectively synthesized dendritic α -Fe₂O₃, γ -Fe₂O₃ and Fe₃O₄ particles via a simple hydrothermal method and reduction-oxide process [13], and discovered that the α -Fe₂O₃ micropine dendrites exhibited a relatively high photocatalytic activity for degradation of VOCs such as gaseous toluene compared with dendritic γ -Fe₂O₃ and Fe₃O₄. This phenomenon demonstrated that the phase transformation-induced crystal plane effect could intrinsically change the surface atomic configuration of the oxide particles and offers another possibility to tune the photocatalytic properties of the semiconductors.

2. Experimental methods

2.1. Sample preparation

α -Fe₂O₃ micropine dendrites were synthesized by hydrothermal reaction of 0.10 mol/L K₃[Fe(CN)₆] in aqueous solutions at 140 °C, which was placed in a Teflon-sealed autoclave and

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maintained at that temperature for 2 d [14]. The red product was isolated by centrifugation, repeated washed with distilled water and absolute ethanol, and dried at 50 °C in air. Reduction for Fe₃O₄ micropine dendrites was achieved by heating at 350 °C for 1 h under a 10 mL/min H₂ and a 120 mL/min N₂ atmosphere. For the preparation of γ -Fe₂O₃ micropine dendrites, the as-prepared Fe₃O₄ micropine dendrites were heated at 150 °C for 2 h in air.

2.2. Characterization

All chemicals were of analytical grade and were used as received without further purification. The as-synthesized products were characterized by an X-ray diffractometer (XRD; Rigaku D/Max 2500), a scanning electron microscope (SEM; JEOL JSM-5610LV) and energy-dispersive X-ray spectroscopy (EDX), transmission electron microscope (TEM; JEOL JEM-2100) with SAED analysis, and X-ray photoelectron spectroscopy (XPS; ESCA PHI5400). The UV–vis spectra of the as-synthesized samples, which were dispersed in pure ethanol at a concentration of around 10⁻³ mol/L and then sonicated at room temperature for 30 min, were recorded on a UNICO 2802PCS spectrometer using a quartz cell (1 cm path length), and pure ethanol was used as a blank [15]. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS55 luminescence spectrometer using a Xenon lamp as the excitation source at room temperature. FT-IR spectra were obtained on a Nicolet Magna 750 FTIR spectrometer at a resolution of 4 cm⁻¹ with a Nic-Plan IR microscope.

2.3. Catalytic activity measurements

Photocatalytic degradation of toluene in air was chosen as the probe reaction to compare the activities of the as-synthesized samples, as toluene is considered as one of the main indoor pollutants as well as the major industrial emissions. The photocatalytic activity tests were performed at room temperature using a steel photo-reactor (\varnothing 7 cm \times 20 cm). The photocatalyst powder was fixed in the center of the reactor by the quartz mesh. The weight of catalyst used for each test was kept at 0.10 g. After the catalyst was placed in the reactor, the reactor was purged by dry air for 1 h. Then, a small amount of toluene was injected into the reactor with a micro-syringe and mixed with dry air. The reactant mixture then flowed through the reactor and allowed to equilibrate at room temperature (25 °C). Once the reactant concentration was stabilized, the inlet and outlet ports were shut off and the 150 W Xe lamp was turned on. The distance between the lamp and sample was about 10 cm. The analysis of toluene concentration (relative error within \pm 1.5%) in the reactor was conducted with a GC-FID (Agilent 7820A, USA). The initial concentration of toluene after equilibrium was controlled at 30 ppmv confirmed by GC-FID. The temperature of the reactor was controlled at 25 °C by continuous cooling air and the RH was controlled at 60%.

3. Results and discussion

3.1. Characterization

The crystallinity, phase and purity of the as-synthesized samples were determined by using the powder XRD method and are shown in Fig. 1a–c. The diffraction peaks of panel (a) in Fig. 1 could be unambiguously indexed to the rhombohedral structure of hematite, consistent with the JCPDS card No. 33-0664. The XRD patterns of the two samples after phase transformation are shown in panels (b) and (c) of Fig. 1. The patterns of panels (b) and (c) of Fig. 1 are almost the same, matching both the magnetite Fe₃O₄ (JCPDS card No. 87-0245) and the maghemite γ -Fe₂O₃ (JCPDS card No. 39-1346). No other peaks corresponding to iron hydroxide or

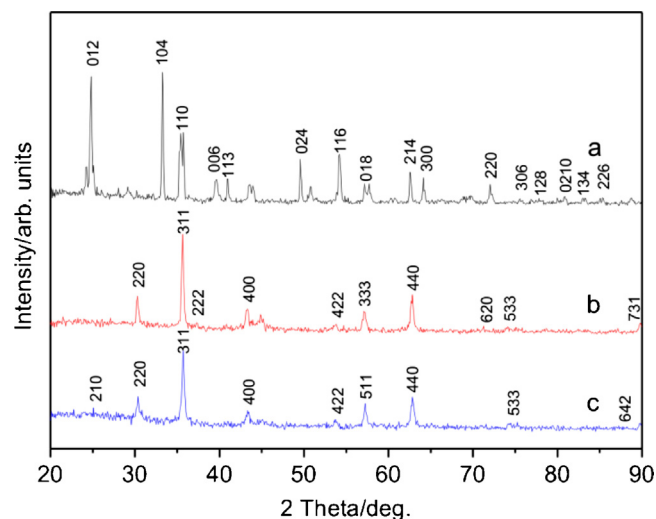


Fig. 1. XRD patterns of the as-synthesized samples: (a) α -Fe₂O₃, (b) Fe₃O₄, and (c) γ -Fe₂O₃.

impurities could be observed. The absence of an iron hydroxide phase confirms that hematite could be directly obtained in this process without any calcinations step for phase transformation. Besides, hematite could be completely transformed into magnetite or maghemite without any other phases in this reduction–oxidation process.

The representative SEM images of the as-synthesized samples are shown in Fig. 2a–f. The dendritic structure of α -Fe₂O₃ has a hierarchical arrangement of a well-defined main trunk, branches and sub-branches as indicated in Fig. 2b. The trunk length is 3–5 μ m, branches are 0.5–1.5 μ m in length and sub-branches are in the range of 100–200 nm. Compared with that of the α -Fe₂O₃ dendrites, we can see that on conversion from α -Fe₂O₃ to Fe₃O₄ and γ -Fe₂O₃ not only the dendritic morphology but also the length of trunk and branches is perfectly maintained as shown in Fig. 2b, 2d and 2f. But, by carefully comparing the scanning electron microscopy of γ -Fe₂O₃ and Fe₃O₄ micropine dendrites with that of α -Fe₂O₃, it is found that the size of the sub-branches is reduced on conversion from α -Fe₂O₃ to Fe₃O₄ and slightly increases on conversion from Fe₃O₄ to γ -Fe₂O₃, respectively. The reason may be that for the conversion from α -Fe₂O₃ to Fe₃O₄, the Fe₃O₄ phase should get rid of some oxygen atoms, resulting in a secondary structure with a reduced size of sub-branches. But the conversion from Fe₃O₄ to γ -Fe₂O₃ involves increasing of oxygen atoms from O₂ to O²⁻ on the surface of sub-branches. There is an evident change in the amount of oxygen element (40.91%, 27.08% and 37.40%, respectively, confirmed by EDX spectroscopy) on the surface of branches as shown in the insets of Fig. 2b, d and 2f.

The TEM images and the corresponding selected area electron diffraction (SAED) patterns of the samples are shown in Fig. 3a–f. The SAED patterns of the α -Fe₂O₃, Fe₃O₄ and γ -Fe₂O₃ micropine dendrites show the single crystalline nature, indicating that the single-crystal nature of the α -Fe₂O₃ micropine dendrites is well preserved after the reduction–oxidation processes. The central spots in the diffraction patterns of Fig. 3b, d and f represent the [000 1], [−1 1 2] and [1 −1 −1] orientations. The other spots representing crystallographic orientations are also marked in the SAED patterns, [1 1 −20], [2 −1 −10], [1 −2 10], and [0 1 −10] for α -Fe₂O₃, [2 20], [1 −1 1], and [3 1 1] for Fe₃O₄, and [2 20], [202] and [0 −2 2] for γ -Fe₂O₃. The trunk and branches of the α -Fe₂O₃ micropine dendrites extend along the six crystallographically equivalent (10−10) directions of rhombohedral α -Fe₂O₃ dendrites, as confirmed by the [0 1 −10] direction in Fig. 3b.

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