

Synthesis and Applications of Hematite α -Fe₂O₃ : a Review

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ABSTRACT

This article reviewed the hematite α -Fe₂O₃. It focuses on its material properties, nanostructures, synthesis techniques, and its numerous applications. Researchers prepared the hematite nanostructure using the synthesis methods such as hydrothermal, and, further, enhanced it by improving the techniques to accommodate the best performance for specific applications and to explore new applications of hematite in humidity sensing.

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I. Introduction

Nano-sized materials and magnetic properties are attracting sufficient attention to scientific interest and have broad application potentials [1], [2]. When the particle is smaller than a nanometer, it changes the magnetic properties and generates new phenomena such as magnetic resistance, superparamagnetism, large coercivity, the decrease of Curie/Neel temperature, and a low or high magnetization [3], [4]. The causes that make the differences are the severance of exchange bonds between atomic surfaces, large surface/volume ratios, surface roughness, and symmetry breaking. It is even more particular for small particles' core induced with antiferromagnetic and ferromagnetic by surface spin to dominate magnetic properties. Given the importance of antiferromagnetic nanomaterial technology, magnetic synthesis systems with nanoscale and crystallinity dimensions attract the attention of researchers.

Many researchers encourage the effort in new methods and exploring new nanostructures to improve the performance of various applications and technologies in the current industry. Hematite (α - Fe₂O₃), as the most stable iron oxide with n-type semiconductor properties (for example = 2.1eV), under ambient conditions attracts scientific and technological interests. Therefore, there needs a study of hematite's effective cost and corrosion as electrode material in photoelectrochemical cells, catalysts, and sensing elements in gas sensors and humidity sensors [5].

This review of nanostructured hematite (α - Fe₂O₃) was different from other studies and previously published works. Some of the things written in this article are the fundamental properties of nanostructured hematite, a summary of the synthesis methods, the potential



options to exploit hematite and further possible improvements using nanostructured hematite.

II. Material Properties

Fe_2O_3 is a ferromagnetic mineral in dark red color and easily contaminated by acids. Fe_2O_3 has various polymorphs of more than one crystal structure forms. The multiple phases of crystal structure in Fe_2O_3 such as α and γ refer to the octahedral coordination geometry, where Fe at the center bounds to six oxygen ligands. The α - Fe_2O_3 , also called hematite, has a rhombohedral structure similar to the corundum structure (α - Al_2O_3). This structure is the most common form in the steel industry. Hematite mineral is as the primary extraction element of naturally occurring iron. The γ - Fe_2O_3 usually occurs as a magnetite mineral with cubic structure. This mineral is metastable and convertible from the alpha phase at high temperatures. The β stage is a cubic body part that is centered, metastable, and equivalent to the alpha phase at temperatures above 500°C (930°F). Fe_2O_3 is an oxide mineral with semiconductor properties through bandgap averaging 2.1 eV and absorbs ~40% of sunlight [5].

III. Nanostructure of α - Fe_2O_3

Studies in hematite's nanostructures consist of various synthesis processes. Nanostructures that grow during the synthesis process depend on factors such as synthesis method, type of precursor, stabilizer, and substrate. Additionally, there are other parameters, including variations in temperature and time during the synthesis process. These nanostructures are benefitting various applications because of their unique structural, optical, and electrical behaviors. The α - Fe_2O_3 nanostructures are nanorod arrays, as shown in Figure 1 [6], hematite-shaped flowers, micro cubes [7], nanowires [8], nanotubes [9], nanoflakes [10], [11], nanoparticles [12], [2], and nanorod arrays [13], [14]. The applications of its nanostructure reach many utilities such as electrochemical photo water separation, gas sensors, photocatalytic, and lithium-ion batteries. Figure 1 shows some morphology of the hematite nanostructures using FE-SEM.

IV. Synthesis of Hematite's Nanostructure

The commonly used main methods in the combination of nanomaterial α - Fe_2O_3 to obtain the desired nanostructures are vapor-phase-based synthesis, deposition, and liquid-phase-based methods. This section only focuses on the most common liquid-based synthesis method and how it changes the morphology and properties of α - Fe_2O_3 . The liquid-phase method in the synthesis of α - Fe_2O_3 includes sol-gel, electrochemical deposition, hydrothermal, and solvothermal. The decision to choose this method is because iron oxide is cheaper, most stable, non-toxic, and environmentally friendly. Among various liquid phase synthesis methods, the synthesis of α - Fe_2O_3 nanostructures commonly uses electrochemical deposition and hydrothermal techniques.

Electrochemical deposition is a process in which the layer of metal, oxide, or salt easily attach to the conductor substrate surface using simple electrolysis of solution contains the desired metal ions or their chemical complexes. Meanwhile, solvothermal is a synthesis technique of single crystals from solutions in thick-walled steel beams (autoclaves). Hydrothermal synthesis is a technique that crystallizes in solution at high temperature and

high pressure. This method produces hematite nanostructures with different morphologies including nanoparticles, microcubes, nanorods, nanorod flower-like and needle-like structures. In most cases, α -Fe₂O₃ hydrothermal synthesis begins with the preparation of a solution containing precursors, stabilizers, and deionization (DI) of water as a solvent. The mixed solution then poured into a Schott bottle or Teflon-line autoclave with high temperature (up to 200°C) for specific hours. After stopping the reaction, the autoclave is cooled naturally at room temperature before continuing to the next characterization step [5].

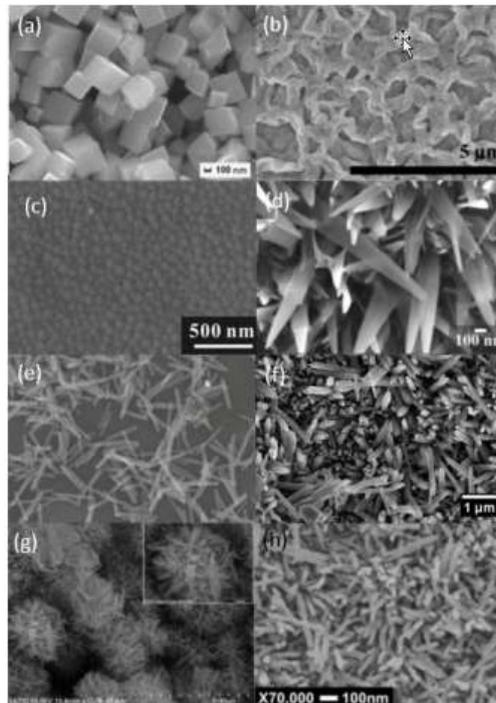


Fig. 1. Nanostructure of α -Fe₂O₃; (a) microcubes, (b) nanowires, (c) nanotube, (d) nanoflakes, (e) nanorods, (f) microstructure orientation, (g) sea-urchin shaped, and (h) worm-shaped

Hydrothermal synthesis influences the formation of nanocrystalline. Particle size increases with reaction time. The reaction time of more than 6 hours gives the maximum particle size at acidic pH, which provides a better condition for growth step with the dehydration process [12]. Other researchers also carried out a similar method where Zn⁺ controlled the formation of α -Fe₂O₃ microcubes with a constant diameter of 250 nm, and the morphological results showed regular structure [15]. Meanwhile, the reaction time after 4 hours did not affect micromorphology.

Furthermore, the reaction temperature did not significantly affect the particle size and shape of the synthesized hematite microcube. The appropriate Zn⁺ ion concentration to control the size and shape of nanostructures accurately formed Zn-doped α -Fe₂O₃. The developed gas sensor shows a high response, good selectivity, and fast recovery time for acetone at a working temperature of 240°C.

Li et al. (2009) grew a single crystal hematite nanorod using direct mixing of 1,2-propane diamine into the solution containing FeCl₃ which was stirred for 15 min. then transferred the slurry mixture to a hydrothermal stainless-steel autoclave. The sample received at 180°C for 16 hours [16]. Mulmudi et al. (2011) obtained hematite nanorods on

a fluorine oxide (FTO) glass substrate using the hydrothermal technique that utilized urea as a pH regulator [17]. In this synthesis, FeCl_3 acted as a precursor and urea acted as the pH regulator. The solution was enclosed in a glass bottle and heated at 100°C for 24 hours. The FTO glass substrate was placed vertically in glass vials with a conductive edge facing the vial wall. After the reaction, the nanostructure on the substrate was thoroughly rinsed in DI water and annealed at 500°C for 30 min. to get the desired phase. The XRD test results revealed a pure hematite phase after annealing at 500°C for 30 min. with incoming direction [110]. Another synthesis declared that hydrothermal in which DI water dissolved the FeCl_3 (0.015 mol) and NaNO_3 (0.1 mol), and the solution that was heated in a closed glass bottle at 100°C for 2 hours produced uniform flower-like architecture with a diameter of 3-5 μm [18]. Each structure consisted of many nanorods in parallel with the average diameter of around 100 nm and an average length of about 900 nm. The structure of the hematite worm nanorods was formed by two steps in-situ annealing at 550°C and 800°C of $\beta\text{-FeOOH}$ nanorods, grown directly on transparent conductive oxide glass [19]. A hollowed porcupine-shaped spines nanostructured hematite obtained by a hydrothermal process using FeCl_3 and Na_2SO_4 as raw material with a temperature treatment of 600°C for 2 hours [20]. The hematite nanostructures consisted of well-averaged nanorods with an average length of about 1 μm growing radially with hollow interiors.

V. Applications of $\alpha\text{-Fe}_2\text{O}_3$

Hematite receives much attention because of its promising characteristics for many applications in electronic, optical, and photonic devices. The interests focus on studies of hematite and hematite as photoelectric chemical solar cell material (PEC) [6], [8], [10], [11], [17], [21], and [22]. Besides, it is a cost-effective, environmentally friendly, and highly efficient approach, also demonstrating chemical stability above a wide pH range suitable for photocatalytic applications [9], [18]. The diameter size and porosity of hematite nanorods also affect the magnetization properties, which are more sensitive in particle less than 20 nm [13]. Also, hematite nanorod was applied to formaldehyde gas sensors (HCHO) and lithium-ion batteries, which proved that the performance of both electrochemical and gas sensor properties is highly dependent on the diameter size and surface area of Brunauer Emmett-Teller (BET). Because of the hollow interior and the meeting point between nanorods, hollowed sea-urchin shaped nanostructures facilitate the diffusion of test gases and improve gas kinetics with oxygen, which shows high gas sensing response, short response and recovery time, and long term stability in detecting ammonia, formaldehyde, trimethylamine, acetone and ethanol [20].

In general, there are two types of humidity sensors: relative humidity sensors (RH) and absolute humidity sensors. Most humidity sensors are relative humidity, classified into three basic types of humidity sensors: humidity sensors based on ceramics, semiconductors, and polymers. Furthermore, absolute humidity sensors are categorized into two classes: solid humidity sensor and mirror-cold hygrometer [23], [24]. Polymer humidity sensors can be divided into two basic categories based on sensing mechanisms: resistive type and capacitive type. Interdigitated electrodes are used to assemble resistive or capacitive humidity sensors. The structure of capacitive humidity sensors generally consists of four layers of different materials. The thin polymeric film acts as a dielectric herb of the capacitor. Changes in relative humidity measured in capacitance are proportional to the polymer/dielectric properties [24]. Therefore, the capacitance value increases when water molecules are absorbed into the active polymer dielectric.

In making this device, there are many attempts to increase the sensitivity of the humidity sensor using various types of nanostructured materials and different engineering techniques. They improve the properties of nanomaterials using SnO₂ [25], TiO₂ [26], CeO₂ [27], and ZnO [28] - [30]. The high sensitivity of the humidity sensor requires a large surface area of nanostructures and better surface morphology for good carrier transportation. The application of relative humidity sensors has been expanded more and more in various fields using these materials, including hematite α -Fe₂O₃ which falls into ceramic (inorganic) materials. The metal oxide-based ceramic type humidity sensor is the most promising material for the application of humidity sensors compared to polymer type-based sensors because of the advantages in mechanical strength, thermal capability, physical stability and resistance to chemical attack. Pelino and Cantalini have reported a review on humidity sensors and the principle, fabrication and application of Si-doped hematite (α -Fe₂O₃) through the sintering method [31] and further analysis of the effect of Silica in hematite [32]. Because of its intrinsic characteristics in mechanical strength and chemical resistance in most environments, ceramics are significant among other materials and are widely used to meet industrial requirements for sensing devices.

The application of pure and doped hematite humidity sensors has been shown to show exceptional moisture sensing properties. Increasing the sensitivity of a hematite-based moisture sensor to metal doping can create surface defects or oxygen voids that increase the adsorption of water vapor through high charge densities. Hematite-based Na⁺ sensors have been found to show a significant response to RH with fast recovery times among other metal ions, such as Li⁺, Mg⁺, Ba⁺, and Sr⁺ [33]. In another study, a group of researchers found that Sr-doped hematite was obtained to achieve sensitivity in 75-100 RH% in air, due to the high porosity of Sr-doped hematite seed, which is suitable for use to measure soil water content [34].

Based on the literature, the α -Fe₂O₃ nanomaterial hematite has not been widely discussed for the application of humidity sensors in many research publications, especially on increasing the sensitivity and transport of carriers in humidity [35]. Therefore, there is a broad view for us to begin the study of the fabrication and characterization of α -Fe₂O₃ nanorod-based humidity sensor arrays to achieve high surface area nanostructures with a high carrier transport.

VI. Conclusions

This article presented an overview of nanostructured hematite (α -Fe₂O₃), which focused on material properties and various nanostructures, specific synthesis methods in hydrothermal techniques, and applications that are useful for current technological demands. Previous studies on the structure of hematite nanorods showed strong potential as a sensing element in humidity sensors. Based on this literature, the humidity sensor is one of the prospective applications that has not been widely studied using the structure of hematite nanorods.

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