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Fe₂O₃ Review: Nanostructure, Synthesis Methods, and **Applications**

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INTRODUCTION

Iron sand is one type of sand containing magnetite iron ore. The iron ore content in this sand gives it unique properties in the form of magnetic properties. When exposed to external magnetic fields, iron sand can exhibit magnetic behavior and even attract metal objects. This phenomenon makes iron sand not only an object of geological exploration, but also a valuable resource in industrial contexts such as, electronics, energy, chemistry, ferrofluids, catalysts, and biomedicine (Aziz, 2021; Basavegowda et al., 2017; Fatih et al., 2021; Mulyani et al., 2022; Nengsih et al., 2023; Puspitaningrum et al., 2017; Susilawati et al., 2018; Tadic et al., 2021; Widodo et al., 2020).

Iron sand contains various magnetic minerals such as α -Fe2O3, FeTiO3, SiO2, Magnetite (Fe, Maghemite) γ -Fe_{203,} Alumina (Al₂O₃), and Rutile (TiO₂). Iron sand can also contain impurities such as clay, non-metallic minerals, or organic material. Iron sand generally has a black or dark brown

color, reflecting a significant magnetite content. The size and shape of iron sand grains can vary this is due to deposition processes such as erosion or transport by water. The characteristics of iron sand may vary depending on the mineral composition and geological conditions in which iron sand is found Kandungan Senyawa Ki (Abdel-Karim & Barakat, 2017; Ibrahim et al., 2022; Tan et al., 2024).

Iron sand can be found in various locations around the world. Iron sand mines are often located in coastal areas, rivers, or lakes that are places of deposition of sedimentary material. In its use, iron sand found in nature needs to be synthesized first to produce pure hematite content (Sismanto et al., 2019).

Current research highlights an innovative synthesis method that can produce nanomaterials from pure hematite. Hematite in the nanoscale has shown unique and distinct characteristics compared to its bulk form. With nanosize, the specific surface area of hematite can increase significantly while maintaining its magnetic properties. The wider surface provides benefits in a variety of applications such as gas sensors, catalysts, lithium-ion batteries, and pigments, and can also be utilized in the manufacture of permanent magnets (Kiswanto et al., 2023; Meijer & Rossi, 2021).

By reviewing the latest literature and research, this review article will compile a comprehensive understanding of the characteristics of iron sand based on the location of its discovery, explore various methods that can be used to produce hematite nanoparticles, and decipher the structure of hematite nanoparticles. Various applications of hematite nanoparticles will also be discussed to determine their development. This article is expected to provide new insights into the potential of iron sand resources and contribute to the development of innovative nanomaterial technologies.

METHODS

This literature research method review will begin by investigating the various literature sources that have been presented to understand the characteristics of iron sand based on the location of its discovery. Consideration will be given to the content of magnetic minerals and impurities in iron sand, as well as variations in grain size and shape affected by the deposition process. Next, research will focus on innovative synthesis methods to produce hematite nanomaterials from iron sand. The analysis will cover the unique characteristics of hematite at the nanoscale, with an emphasis on increasing the specific surface area and maintaining its magnetic properties. This article will compile a comprehensive understanding of the structure of hematite nanoparticles and present various applications of hematite nanomaterials, such as gas sensors, catalysts, lithium-ion batteries, and permanent magnet manufacturing. This literature review is expected to provide new insights into the potential of iron sand resources and contribute to the development of innovative nanomaterial technologies, especially in the context of water treatment, catalysis, and energy storage.

RESULTS

Coastal Areas

Coastal areas are known as places where the process of material deposition by seawater occurs. The deposition of material by seawater will affect the concentration of iron minerals. Therefore, iron sand in coastal areas has a high iron content. In addition to iron minerals, iron sand in coastal areas can also contain additional minerals such as ilmenite, magnetite, or other metal minerals. Comparison of iron sand characteristics of coastal areas in Indonesia can be seen in Table 1 (Bahfie, 2022; Kotarumalos et al., 2023).

Iron sand in coastal areas occurs due to rocks containing iron minerals eroded by sea waves and carried to the coast. In addition, the process of weathering and erosion also plays a role in forming iron mineral particles that are free from the original rock. The accumulation of iron sand along the coast or coastline occurs with the help of tides (Setiady et al., 2020).

Table 1. Comparison of iron sand characteristics of coastal areas in Indonesia

River

Iron sand in rivers generally has varying grain sizes, depending on the process of transportation and deposition by water. The size of sand grains in rivers is usually smaller than the size of sand grains in coastal areas. This can occur due to the process of transportation by water until it arrives at the river can break the grain. The color of iron sand in rivers can vary, but usually has a brighter color than the color of iron sand in coastal areas (Didik et al., 2020; Nugroho & Basit, 2014).

Iron sand is often unevenly distributed along river flows due to the deposition process. The deposition process can lead to the deposition of iron sand in certain areas such as, river bends and prominent plains along the flow. In addition, strong river currents can transport and precipitate different iron particles in different parts of the water flow. The iron sand content in the river has impurities such as clay, non-metallic minerals, or organic material (Kamiludin et al., 2016).

Location Name	Dominant Minerals	Additional Minerals	Physical, Mechanical, and Chemical Properties	Reference
Batang Kuranji River, West Sumatra	Albite, magnetite	Quartz, halloysite, saponite, and	Ferromagnetic minerals	&; (Afdal Niarti,
		pyrophyllite		2013)
Central Lampung	Ilmenite, and Potassium Chloride	Not explained further	Antiferromagnetic	(Puspitarum et al., 2019)
Tor River, Papua	Magnesioferrite	Augit-aluminian	Magnetization is high saturation, and coercive field is low.	(Togibasa et al., 2018)
Sompang River, East Lombok	Silica	Aluminum, Carbon, Sodium, and Potassium	It is finely grained, and has a smaller size than river sand	(Meiliyadi et al., 2022)
Bah Bolon River,	Magnetite,	Titanium, Aluminum,	It is soft magnet, and high	(Novita) et
North Sumatra	Hematite, and Maghemite	Copper. Manganese, Silica, Vanadium	saturation.	al., 2023)

Table 2. Comparison of the characteristics of river iron sand in Indonesia

Based on research that has been done, the mineral content in iron sand in rivers has a more unique diversity than the mineral content in iron sand in coastal areas. This can occur because the iron sand in the river has mixed with various minerals during the transportation process by water.

Hematite Nanostructure (α-Fe2O3)

Hematite $(\alpha$ -Fe2O3) has properties that are difficult to corrode so it is suitable for applications such as gas sensors, catalysts, lithium-ion batteries, and pigments, it can also be used in the manufacture of permanent magnets. At high temperatures, the α -Fe (Edianta et al., 2021; Gandha et al., 2016; Miftahul Khoiroh et al., 2013; Rostami et al., 2021; Suhendi et al., 2021; Susilawati et al., 2022). (hematite) phase is the most stable phase compared to other phases. This crystal structure is rhombohedral (trigonal) with a crystal type such as corundum (α -Al2O3), has a space group "R-3 c" lattice parameters $a = b = 5.036$ Å, $c = 13.747$ Å, $\alpha = 90^\circ$ (Figure 1). It is antiferromagnetic under \sim 260 K (Morin transition temperature), and weak ferromagnetic between 260 K and 950 K (Neel temperature). Many factors, such as pressure, particle size, and magnetic field intensity influence its magnetic properties. Fasahematite has curie temperatures above 800 $^{\circ}$ C and below 1000 °C (Song & Pistorius, 2019).

Figure 1. (a) Corundum structure of hematite $(\alpha$ -Fe₂₀₃); (b) Rhombohedral shape of **hematite crystal lattice (α-Fe₂₀₃)**

IJSSR Page **542**

To produce α -Fe 203 nanoparticles is carried out using several methods, including the solgel method, from which the particle size of α -Fe2O3 between 10 – 20 nm, the hydrothermal method with a particle size of 30 nm, the ball miling method, with a particle size of 99.14 μ m – 93.34 μ m, and the coprecipitation method, with a particle size of 22.8899 nm (Dewi & Adi, 2018; Fahlepy et al., 2019; Gandha et al., 2017; Malik & Putra, 2018; Tadic, Panjan, et al., 2019)

Various nanostructures have been studied on hematite by varying the synthesis process. The nanostructures formed during the synthesis and fabrication process also depend on different factors such as synthesis methods, types of precursors, stabilizers, substrates, and not to mention their parameters, for example, temperature and time variations in the synthesis process. Nanostructures are useful for a wide range of applications due to their unique structure and optical and electrical behavior. The nanostructure of α -Fe2O3is nanorods, as shown in Figure 2, microcubes, nanowires, nanotubes, nanoflakes, flower-shaped hematite, nanoparticles, and nanorod arrays (W. R. W. Ahmad et al., 2017, 2019; Atabaev, 2015; EmiL-Kaya et al., 2022; Gurudayal et al., 2014; X. Li et al., 2015).

Figure 2. Nanostructure of α -Fe2O3; (a) microcubes, (b) nanowires, (c) nanotubes, (d) nanoflakes, (e) nanorods, (f) microstructure orientation, (g) sea-urchin shaped, and (h) **worm-shaped.**

Hematite nanostructure synthesis Coprecipitation

Iron sand is separated by impurities using neodymium magnets. The result is then dissolved into HCl, with the reaction:

$$
Fe2O3 + 6HCl \rightarrow 2FeCl3 + 3H2O
$$

Stirred and heated at 80oC using a magnetic stirrer at a speed of 350 rpm for 2 hours. Precipitation is carried out by dripping ammonium hydroxide (NH_4OH) dissolved to pH 6 and forming a precipitate by the reaction:

 $2FeCl3 + 3H2O + 6NH4OH \rightarrow 2Fe (OH)3 + 6NH4Cl + 3H2O$

The resulting precipitate is washed with equates and dried in a memmert oven at 100° C for 19 hours, with the reaction:

2Fe (OH)3+6NH4OH+3H2O→ 2FeOOH+6NH4Cl+5H2O

The dried sample is ground and then calcined. The synthesis process using the coprecipitation method can be seen in Figure 3. The weakness of the coprecipitation method is that the grain size distribution of nanoparticles tends to be large, as well as the polydisversiveness of small particles. Nanoparticles are easily agglomerated the synthesis of nano-hematite using the coprecipitation method has been reported in various studies. A comparison of the results of each study that has been conducted can be seen in Table 3.

Figure 3. Flow of the coprecipitation method/*Kushwaha &; Chauhan, 2021*)

Gel Insoles

The sol-gel method is a synthesis method that requires chemical engineering. The term solgel comes from two words, namely: 1) sol refers to a precursor solution that will be used as the starting material for the synthesis of Fe2O3 nanoparticles; and 2) gel refers to the form of the final product of synthesized nanoparticles in the form of gels. The sol-gel method is commonly used to synthesize ceramic materials and is not suitable for synthesizing oxide nanoparticles, so additional modifications are needed in using this method. The sol-gel method is a chemical method that has a complex procedure. Many synthesis parameters must be observed (Indrayana, 2019).

Table 4. Process Parameters of Gel Soles

The sol-gel method has several disadvantages, namely: 1) it produces a lot of alcohol during the calcination process, 2) it requires additional heat treatment at high temperatures, and 3) the nanoparticle permeability is high, and the bonding power of nanoparticles is weak (Koo et al., 2019)

Hydrothermal

Hydrothermal is formed from the words hydro which means water and thermal which means heat. So the hydrothermal method is a method that uses water and heat whose properties convert solutions into crystals. The hydrothermal method must be performed in a closed system to prevent solvent loss when heated above its boiling point (Jung et al., 2018; Noviyanti et al., 2012; Ou et al., 2018; Qiongyu Li, 2018a; C. Wang et al., 2018; W. Wang et al., 2018; G. T. Zhu et al., 2018).

Hydrothermal synthesis is widely used in the manufacture of metal oxides. Metal oxide synthesis can occur in two stages. The first stage is hydrolysis of the salt solution to produce metal hydroxide. The second stage is that the hydroxide will be dehydrated to produce the desired metal.

Water is the most effective solvent in dissolving ionic compounds at high temperatures and pressures. Water can also act as a pressure transmission and as a precursor solvent, so the resulting powder can be amorphous or crystalline. The advantages of the hydrothermal method include being able to produce crystalline products that can be achieved at low enough temperatures with a high degree of crystallity, can reduce agglomeration between particles, can produce a relatively uniform particle size distribution, high product purity, relatively cheaper, directly formed powder from solution, shape and particle sizes can be controlled from the initial material and different hydrothermal conditions, The reactivity of the resulting powder is high, and allows the synthesis of compounds that have oxidation numbers that are difficult to obtain, especially transition groups (Colombo et al., 2015; Fulle et al., 2018; Zarringhadam & Farhadi, 2018).

In addition, hydrothermal also has a drawback, that is, the initial solubility must be known, hydrothermal slurry is corrosive, and the use of high-pressure vessels will be dangerous in case of accidents (Mercier et al., 2018; D. F. Putri et al., 2019).

Figure 4. The process of synthesis of hydrothermal methods with various precursors(Kongsat et al., 2021)

Good crystals can be obtained by adding a mineralizer. Mineralizer serves to increase the polarity of water to increase the solubility of a dissolved substance. Compounds used as mineralizers should not be seen in reactions, and commonly used compounds are alkaline bases, NaOH, and KOH (Noviyanti et al., 2018).

Hydrothermal	Particle Size and	Physical, Mechanical, and	Influence of Process	Ref.
Variations	Shape	Chemical Characteristics	Parameters	
Anionic, cationic,	Spherical particle	Single-domain magnetic	The type and	(Kongsat
and nonionic	shapes with a	behavior, coercivity of 225	concentration of	et al.,
surfactants.	diameter ranging	Oe, high stability, and	surfactants can affect the	2021)
Temperature 180 ^{oC.}	from 15-205 nm.	thermal conductivity of	colloidal stability and	
		$0.4787 W/mK$.	thermal stability of	
			nanoparticle	
			suspensions.	
PVP surfactants and	The average	The highest capacitance is	The concentration of the	(M. Zhu et
NaAc precipitants.	particle size is 40	340.5 F/g at a current	precursor affects the	al., 2012)

Table 5. Comparison of research results using hydrothermal methods

International Journal of Social Service and Research, Novita¹, Ramlan², Marzuki Naibaho³, Masno Ginting⁴, Syahrul Humaidi⁵, Tulus Na Duma⁶

Sonication

The sonication method is the easiest and most effective method for large-scale production with precise size control, high morphology, and crystallinity. In research using ultrasonic sonochemical methods obtained polyhedron monodispersa hematite nanoparticles with uniform shape, particle size of about 14nm at a temperature of 500°C (Khalil et al., 2017). Shock waves in the sonification method can separate the agglomeration of a particle (agglomeration) and due to the influence of sonification (ultrasonic) can produce nanoscale crystal sizes. This method uses ultrasonic bath with high frequencies such as 20 kHz - 10 MHz to break down metal ions in molecules so that it is expected that the crystal growth process can take place quickly and can avoid oxidation of metal ions resulting in the formation of amorphous particles (Candani et al., 2018; Firnando & Astuti, 2015).

Figure 5. Synthesis process sonication method (Fuentes-García et al., 2020)

Applications of Hematite (α-Fe2O3) Nanoparticles

Hematite nanoparticles $(\alpha$ -Fe2O3) have potential applications in various fields of advanced nanotechnology, such as electronics, optical devices, photonics, and microwave absorbers. Much research has focused on hematite nanoparticles $(\alpha$ -Fe2O3) both undoped and doped as solar photoelectrochemical cell (PEC) materials (Bai et al., 2022; Dhiman et al., 2020; Kamil et al., 2022; Y. Li et al., 2021; Silva et al., 2020).

Hematite nanoparticles $(\alpha$ -Fe₂O₃) are also suitable for photocatalytic applications because they are environmentally friendly, cost-effective, and have chemical stability over a wide pH range. The size of the diameter and porosity of the hematite nanorod (ALP, 2023; S. A. Putri et al., 2021; Suchi Ramadhani Putri et al., 2022). α -Fe2O3 also affect the magnetization properties. Furthermore, hematite nanorods (α-Fe2O3) (Rifai et al., 2021; S., 2019; Simbolon et al., 2021; Sinuhaji et al., 2021) are also applied to gas sensors and Lithium-ion batteries, where it has been proven that the working principle of electrochemical and gas sensors is highly dependent on the size of the diameter and surface area of the Branauer Emmet-Teller (BET) (A. Ahmad et al., 2019; Hung et al., 2016; Indra & Noerochim, 2016; Liu et al., 2020; Ma et al., 2020; Qin et al., 2022).

Hematite nanoparticles $(\alpha$ -Fe2O3) can also be applied as microwave absorbers on aircraft walls. By utilizing the potential of natural sand in East Java, a prototype of a microwave absorbing coating based on Mhexaferite BaFe12-xZnxO19 has been successfully made, by making it a coating for paint composite materials on the interior walls of the aircraft. The use of hematite nanoparticles as microwave absorbers is also supported by the results of research conducted by Rianna et al using natural iron sand (Efhana et al., 2013; Rianna et al., 2023).

Barium hex ferrite is an ideal material to dampen electromagnetic interference (EMI) caused by malfunctions in electronic equipment. One of the ingredients for making Barium hexaferrite is hematite $(\alpha$ -Fe2O3) (Susanto et al., 2014). Barium hexaferrite has been widely studied because it has many advantages, including its relatively cheap price, high curie temperature, resistance to corrosion, good physical properties, and its manufacture is relatively easy (Dermayu Siregar & Humaidi, n.d.; Hayati et al., 2016; Widanarto et al., 2015).

Hematite nanoparticles as water and sewage treatment have been reported in research by Kefeni et al. Based on the research that has been done, hematite nanoparticles have succeeded in removing Al, Mg, Mn, Zn, Ni, Ca, and Na metals. The adsorption and precipitation properties possessed by hematite can help in the process of cleaning water from heavy metals and other solutes. This is also reinforced by the findings of Aal et al which show that hematite nanoparticles can absorb Cu, Ni, Co, Cd, and Pb ions (Abd El Aal et al., 2019; Kefeni et al., 2018).

In the medical field, hematite nanoparticles also show no less unique abilities, one of which is their use as a delivery drug. Hematite nanoparticles can be coated with drug compounds to be then directed to specific locations in the body using external magnetic fields. External magnetic fields can also generate heat through magnetic hysteresis in magnetic hyperthermia therapy to damage cancer cells. In addition, the unique magnetic properties that hematite nanoparticles possess can help in medical imaging techniques such as magnetic resonance (MRI) by increasing image contrast (Beato-López et al., 2020; Mabrouk et al., 2020; Pham et al., 2016; Surowiec et al., 2017).

Figure 6. Applications and methods of synthesis of hematite nanoparticles (Kokila et al., 2022)

CONCLUSION

Based on the literature that has been described, it can be concluded that iron sand can be further utilized in producing a variety of minerals, especially hematite. The characteristics of iron sand used can be influenced by the location where iron sand is found. In addition, the synthesis method plays an important role in determining the physical, mechanical, and chemical properties of hematite nanoparticles from iron sand. The structure of hematite nanoparticles, especially at the level of crystallinity and surface morphology has an impact on the performance and application of hematite nanoparticles. Hematite nanoparticles have demonstrated their capabilities in a wide range of applications, including water and environmental treatment, catalysts, and energy storage.

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