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Review

Progress in electrochemical synthesis of magnetic iron oxide nanoparticles

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ABSTRACT

Recently, magnetic iron oxide particles have been emerged as significant nanomaterials due to its extensive range of application in various fields. In this regard, synthesis of iron oxide nanoparticles with desirable properties and high potential applications are greatly demanded. Therefore, investigation on different iron oxide phases and their magnetic properties along with various commonly used synthetic techniques are remarked and thoroughly described in this review. Electrochemical synthesis as a newfound method with unique advantages is elaborated, followed by design approaches and key parameters to control the properties of the iron oxide nanoparticles. Additionally, since the dispersion of iron oxide nanoparticles is as important as its preparation, surface modification issue has been a serious challenge which is comprehensively discussed using different surfactants. Despite the advantages of the electrochemical synthesis method, this technique has been poorly studied and requires deep investigations on effectual parameters such as current density, pH, electrolyte concentration etc.

1. Introduction

1.1. Iron oxide phases and its properties

Iron oxides are classified as the substantial transition metal oxides taking advantage of technological importance. In nature, iron oxides can be found in many different forms [1]. Sixteen pure phases of iron oxides, particularly, oxides such as Magnetite, Hematite, Iron oxide beta phase and Maghemite, hydroxides such as Iron(III) hydroxide or Bernalite, Iron(II) hydroxide, oxyhydroxides such as Geothite, Akaganetite, Lepidocrocite, Feroxyhyte are known to date. Trivalent state, distinct colors and low solubility are characteristics of these compounds [2]. Among entire iron oxides and hydroxides, only Schwertmannite (iron-oxyhydroxysulfate) and ferrihydrite (hydrous ferric oxyhydroxide) are poorly crystalline.

One of the most important iron oxide, black in color and ferromagnetic, is Magnetite (Fe_3O_4) which contains both Fe(II) and Fe(III). Although stoichiometric magnetite has Fe(II)/Fe(III) equals to 0.5 but magnetite, which is frequently non-stoichiometric results in a Fe^{3+} deficient layer. Magnetite has an inverse spinel crystal structure with a face-centered cubic unit cell having an edge length of 0.839 nm and 32 oxygen atoms. In this particular crystal structure Fe^{2+} and half of the Fe^{3+} occupy octahedral sites and the other half of the Fe^{3+} occupies tetrahedral sites. Divalent iron atoms prefer to take octahedral sites to obtain higher crystal field stabilization energy. However, the trivalent iron atoms occupy the two octahedral and tetrahedral sites (crystal field stabilization energy=0). The actual crystal types of magnetite consist of octahedron and rhombodecahedron with surface area in the range of 4 to100 $m^2\,g^{-1}$ [3].

The second important and common iron oxide is hematite (α-Fe_2O_3). Hematite is iso-structural with corundum (α-Al_2O_3), consisting of a dense arrangement associated with Fe^{3+} ions in octahedral coordination with oxygens in hexagonal closest-packing. The crystal system of hematite is hexagonal with the lattice parameters of a=5.0346 Å, c=13.752 Å, however crystals include lots of forms. The structure can be also ascribed as the stacking of Fe^{3+} ions sheets between two closed-packed layers of oxygens, holding together by covalent bond. The structure in addition has a three-dimensional framework developed along with trigonally distorted octahedra FeO_6, linked to thirteen neighbors by one face, three edges and six vertices. Because Fe is in a trivalent state (ferric Fe), each one of the oxygens is actually bonded with just two Fe ions, and so, only two out of three available oxygen octahedrons are occupied. This specific arrangement tends to make the structure neutral with no deficit or charge excess. Hematite's specific surface area ranges from 10 to 90 $m^2\,g^{-1}$ [3].

Goethite, common form of iron oxy-hydroxide, α-FeO(OH) exhibits an orthorhombic crystal structure with lattice parameters of a=9.95 Å, b=3.01 Å, c=4.62 Å. This structure is a three-dimensional

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structure built up with $FeO_3(OH)_3$ octahedra forming large tunnels, spreading out along the direction (0 1 0) whereas hydrogen atoms are positioned. Each octahedron is linked to eight neighboring octahedral by four edges and three vertices. Oxygen atoms are in tetrahedral surroundings, either OFe_3H or OFe_3H (bond). Goethite can be found in different shapes and morphologies; however, its morphology mostly is acicular. Its specific surface has been reported from 8 to 200 $m^2\,g^{-1}$ [3].

Ferrihydrite is generally accustomed to explain both 2- or 6-line ferrihydrite, which have either two or six identifiable broad reflections in a diffraction pattern. Ferrihydrite has different chemical formulae, including $Fe_5HO_8 \cdot 4H_2O$, $Fe_5(O_4H_3)_3$, $Fe_2O_3 \cdot 2FeOOH \cdot 2.6H_2O$ and $5Fe_2O_3 \cdot 9H_2O$ [4]. The shape of ferrihydrite is spherical and unlike other iron oxide phases it forms only as nano crystals representing high specific surface areas in the range of 100 to 700 $m^2\,g^{-1}$ [3]. The structure of ferrihydrite continues to be controversial as the lowest degree of order hinders the clarification of the structure.

Wüstite (FeO) is another phase of iron oxide with a cubic unit cell. This phase is stable under thermal equilibrium at high temperatures (above 843 K) and low pressures. The large O^{2-} anions form a close packed fcc sublattice with the small Fe^{2+} cations which occupied the interstitial sites. Just about all Fe ions are octahedrally coordinated to oxygen [5]. In Wüstite, the oxygen and iron (1 1 1) planes form ideal two-dimensional hexagonal lattices with an inter-atomic distance of 3.04 A, which usually corresponds to the lattice constant of the hexagonal unit cell on the unreconstructed FeO(1 1 1) surface. Along the (1 1 1) direction the iron and oxygen (1 1 1) planes form the cubic ABC stacking sequence with an interlayer distance of 1.25 A. The length of the iron–oxygen bond is 2.16 A.

Akaganeite (β-FeOOH) is an iron oxyhydroxide phase with largest tunnel-type structure among all other phases. In this structure, iron atoms are powerfully bonded to the framework. In akaganeite the octahedral sites are generally occupied by FeH and Cl and perhaps H_2O is presumably located in the tunnels (Cl^- is considered as an impurity) [6].

Lepidocrocite (γ-FeO(OH)) with crystal structure of Orthorhombic, is assembled by double layers of Fe-octahedra, and hydroxyl groups which occupied their external surfaces and allowing the formation of hydrogen bonding between the layers. It is believed that hydrogen atoms are located at the centers of inversion and occupied the same distances from two oxygen atoms of the adjacent layers, therefore producing continuous O–H–O–H–O chains with hydrogen bonds symmetry. The main morphology of lepidocrocite is either lath-like or tabular and the surface area are usually between 15 and 260 $m^2\,g^{-1}$ [3]. Table. 1 summarizes all information regarding to iron oxide different phases and properties.

1.2. *Applications of iron oxide nanoparticles*

Iron oxide nanoparticles are widely used as highly active catalysts which have been applied in several oxidation/reduction and acid/base reactions [7]. Iron oxide-based materials are counted to be cheap and efficient candidates in environmental catalysis. Recent synthetic advances have resulted in iron oxide nano-particles are considerably more effective than conventional larger-sized iron oxide [8,9] for the oxidation of carbon monoxide and the oxidative pyrolysis of biomass [9] or biomass model compounds [10,11]. The reason can be explained based on the fact that nanoparticles have the enhanced surface area ratio and more coordination of unsaturated sites on their surfaces which leads to their higher activity. Moreover, matrix supported nanoparticles, which have indicated improved stability have found a broad application as catalysts. Magnetite and hematite are the most common catalysts were employed among all types of iron oxides. In addition, catalytic activity of heterogeneous catalyst with iron oxide and heterogeneous catalyst based on magnetic mixed iron oxides has been widely investigated [12]. For instance, $Li_xCu_{1-y}Fe_yO$ [13,14] nanoparticles have been assessed as potential components of lithium-ion batteries.

Magnetic nanoparticles were also explored for their potential application as high-density magnetic data storage. If a single nanoparticles with size of 5 nm can storage individual bit of information, so storage density of 10 Gbit cm^{-2} would not be impossible [15]. Magneto-optical switches are another application of iron oxide nanoparticles. They have also revealed which are applicable in sensors based on giant Magnetoresistance [16–18], magnetically controllable Single Electron Transistor devices [19–21] and photonic crystals [22].

Dilute magnetic semiconductors (DMS), which have recently attracted lots of attention, is doped iron ions into the semiconductors to optimize the optical and electronic properties of magnetic nanoparticles and semiconductors [23]. DMS nanoparticles can be applied in the production of novel optical materials. Additionally, DMS nanoparticles show strong photoluminescent emission of green light [18]. Moreover, the electronic characteristics of DMS nanoparticles sense both light and magnetic fields that represent their functionality in the magneto-optical switches' fabrication [24,25].

Magnetic iron oxide nanoparticles have also displayed a large number of biomedical applications; the most common application is considered in Magnetic Resonance Imaging (MRI) as contrast agents [26–29]. Researchers were able to develop bio-conjugated magnetic iron oxides which involved targeting of MRI probes towards the brain tumors along with its real-time monitoring [30]. Drug delivery or Magnetic drug targeting has been recently focused on application of iron oxide nanoparticles as carriers, which preventing the conventional chemotherapy side effects and representing a promising cancer cure.

Iron oxide nanoparticles are also able to nucleate and control the high aspect ratio nanomaterials growth like carbon nanotubes (CNTs), where a substrate is coated with iron nanoparticles and CNTs are thereby grown applying various chemical vapor deposition processes. Nanoparticles of irons and its compounds [31–33] have shown their reactivity in the mentioned processes. In the case of iron nanoparticles, the diameter of CNT can be controlled in the range of 3–13 nm by the diameter of the nucleating iron nanoparticles [34].

Iron oxide nanoparticles can be utilized to remove toxic waste. Bulk iron oxide can act as reducing agent and decompose various toxic chemicals and compounds in aqueous solutions [35,36]. As mentioned before, due to large surface area, nanoparticles are more efficient at wastewater treatments, for instance iron nanoparticles could remove Cr^{4+} and Pb^{2+} from aqueous solutions [37].

A Large amount of synthetic (63%) and natural (37%) iron oxides is used as pigment world-widely. The commonly used iron oxides such as goethite, magnetite, maghemite and hematite are applied as pigments to produce yellow, black, brown and red colors, respectively. Reduction in the particle size and achieving nano-sized particles assist to obtain transparent iron oxide pigments.

Several studies have been concentrated on γ-Fe_2O_3 (Maghemite) and β-Fe_2O_3 phases, indicates suitable sensing characteristics towards carbon monoxide, hydrocarbon gases and alcohol [38–44] and therefore can be employed in gas sensing applications.

Iron oxides have extensive applications as pigments, catalysts, coatings, lubrication, ion exchangers, sorbents, and gas sensors [45–50]. Moreover, Iron oxide nanoparticles and nanocomposites have potential applications in different areas like magnetic data storage devices, magnetic recording, inks and toners for xerography,