Progress in the Preparation of Magnetite Nanoparticles through the Electrochemical Method†

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Abstract

Magnetite (Fe₃O₄) is one of the most important iron oxides due to its extensive range of application in various fields. The characteristics of magnetite can be considerably enhanced by reducing the particle size to the nanometer scale. When novel functions of nanoparticles are desired, it is necessary to have monodispersed or nearly monodispersed nanoparticles. Many synthesis methods have been proposed to produce monodispersed magnetite nanoparticles, including co-precipitation, sol-gel, hydrothermal and electrochemical methods. In this review, progress in the preparation of magnetite nanoparticles and their composites through the electrochemical method and the scale-up method are discussed.

Keywords: magnetite nanoparticles, electrosynthesis, scale-up, monopolar, particle formation, precipitation

1. Introduction

Magnetite (Fe₃O₄) is one of the most important iron oxides, a common compound that is widespread in nature and readily synthesized in the laboratory and is widely used in industry. Magnetite is a black, ferrimagnetic mineral containing both Fe(II) and Fe(III). Other names are recognized for magnetite, including black iron oxide, magnetic iron ore, iron(II, III) oxide, loadstone (when natural polarity is present), tri-iron tetroxide, ferrous ferrite and Hercules Stone. Although several of the names are not recognized as mineral names, they are in current use. The names reflect the diversity of disciplines for which this mineral is of interest.

Magnetite is a magnetic material and contains many exciting properties and potential for various applications. Magnetite particles have been used in data storage and improved electronic devices (Sharrock M.P. and Bodnar R.E., 1985). These particles also have considerable potential for use in the biomedical industry, such as targeted drug delivery, hyperthermia treatment, cell separation, magnetic resonance imaging, immunoassays and the separation of biomedical products (Jain T.K. et al., 2005; Mahmoudi M. et al., 2011; Qiao R. et al., 2009). Magnetite particles are also used as active catalysts for several oxidation/reduction and acid/base reactions and as an efficient candidate in environmental catalysis (Jin X. et al., 2012; Moghanian H. et al., 2014). The catalytic activity of magnetite can be considerably enhanced by reducing the particle size to the nanometer scale. It has been demonstrated that magnetite nanoparticles exhibit high catalytic activity for the esterification of oleic acid with methanol in the production of methyl oleate (biodiesel) (El-Nahas A.M. et al., 2017). These particles can also be used as promising electrode materials for electrochemical energy storage systems, such as Li-ion batteries and supercapacitors (Cheng J. et al., 2012; Liu J. et al., 2013).

Magnetite is naturally found in the form of an iron ore containing a significant amount of impurities. The iron ore must be processed to obtain higher purity of magnetite having specific properties suitable for various applications. The synthesis of magnetite nanoparticles is complicated because of their natural colloidal behavior. The most common method to synthesize magnetite nanoparticles is the co-precipitation of ferric and ferrous ions in highly basic conditions (Petcharoen K. and Sirivat A., 2012; Shen L. et al., 2014). The formation of magnetite is in favor in the pH range of 8 to 14 along with a Fe³⁺/Fe²⁺ ratio of 2:1 under non-oxidizing conditions (Ramimoghadam D. et al., 2014). The formation of magnetite is in favor in the pH range of 8 to 14 along with a Fe³⁺/Fe²⁺ ratio of 2:1 under non-oxidizing conditions (Ramimoghadam D. et al., 2014). The advantage of this technique is its capability for a high production rate of magnetite nanoparticles. Controlling particle size distribution is, however, inconvenient due to the immediate reactions in the mixture that make it difficult to control the crystallization process. Hydrothermal and sol-gel methods are among the most well-known techniques, as well as co-precipitation, for
the production of magnetite nanoparticles with controlled morphology and chemical composition (Daou T.J. et al., 2006; Han C. et al., 2012; Haw C.Y. et al., 2010; Lemine O.M. et al., 2012; Xu J. et al., 2007). In the hydrothermal technique, reactions are carried out in aqueous media at high pressure and temperature. The size and shape of the nanoparticles can be controlled by manipulating the reaction time, temperature, reactant composition, solvent type and surfactant (Daou T.J. et al., 2006; Han C. et al., 2012).

Depending on the synthesis method and conditions, synthetic magnetite may have different morphologies and crystal structures. The hydrothermal method usually produces magnetite with octahedral crystals, but it grows to have a combination of rhombic dodecahedral crystals in the presence of mineralizers (Qu X. et al., 2010). Synthesis in aqueous systems at temperatures less than 100 °C produces rounded magnetite having cubic or octahedral crystals. For example, octahedral and spheres are obtained by oxidizing green rust with KNO₃ at 90 °C and pH 6–10. Spheres are formed when Fe²⁺ > OH⁻, but they change into cubic crystals in excess OH⁻ (Thapa D. et al., 2004). Divalent iron may be partly or entirely substituted by a broad range of other divalent ions because of the availability of tetrahedral and octahedral positions. The substitution ions can be fitted well into the structure due to the flexibility of the oxygen framework, which can accommodate the cations of different sizes. The ion is accompanied by changes in the length of unit cell edge. The products in which the Fe(II) is fully substituted by another divalent ion M(II) to form MFe₂O₄ are known as ferrites. There has been considerable interest in ferrites themselves, owing to their applications in, for instance, electrical appliances and as catalysts (Galindo R. et al., 2012; Mazario E. et al., 2013).

### 2. Magnetite properties

#### 2.1 Bulk properties

The general properties of magnetite are presented in Table 1 (Cornell R.M. and Schwertmann U., 2003). The naturally occurring and synthesized magnetite crystals exhibit metallic luster and opaque black color. The density is approximately 5.18 g/cm³, lighter than pure iron (α-Fe; 7.87 g/cm³). The hardness is approximately 5.5, identical to glass. Magnetite particles are non-porous with surface areas that vary according to synthesis method. Different methods generate different particle sizes, and in turn, different surface areas. The standard free energy of formation is –1012.6 kJ mol⁻¹, indicating that magnetite formation is thermodynamically favorable. Magnetite is soluble under acid conditions (Setyawan H. et al., 2012). The solubility product is dependent on the appropriate dissolution reaction.

The crystal structure of magnetite follows an inverse spinel pattern with a face-centered cubic cell based on 32 O²⁻ ions, which are regularly cubic close-packed along the [111]. The unit cell has eight formula units per unit cell with a length edge of 0.839 nm. Magnetite contains both divalent and trivalent iron and is frequently non-stoichiometric, i.e., it has a cation-deficient Fe(III) sublattice. The divalent iron species occupy half of the octahedral lattice sites due to higher crystal field stabilization energy. Conversely, the trivalent iron species occupy the other octahedral lattice sites and all tetrahedral lattice sites. The octahedral and mixed tetrahedral/octahedral layers stacked along [111] (Cornell R.M. and Schwertmann U., 2003).

The melting point of magnetite ranges from 1583 to 1597 °C, and its boiling point is 2623 °C. The heat of fusion, decomposition, and vaporization are, respectively, 138.16, 605.0 and 298 kJ mol⁻¹.

The Curie temperature of magnetite is 850 K. Below that temperature, magnetite possesses ferrimagnetic behavior. In this case, magnetic moments on tetrahedral sites, occupied by Fe(III), are ferromagnetically aligned, while magnetic moments on octahedral sites, occupied by Fe(III) and Fe(II), are antiferromagnetic and cancel each other out. When the Curie temperature is attained, net magnetization is zero, and magnetite possesses super-paramagnetic behavior.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>General properties of magnetite.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
<td></td>
</tr>
<tr>
<td>Crystal structure</td>
<td>cubic</td>
</tr>
<tr>
<td>Cell dimension (nm)</td>
<td>a = 0.8396</td>
</tr>
<tr>
<td>Formula units, per unit cell, Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (g cm⁻¹)</td>
<td>5.18</td>
</tr>
<tr>
<td>Color</td>
<td>black</td>
</tr>
<tr>
<td>Hardness</td>
<td>5 ½</td>
</tr>
<tr>
<td>Type of magnetism</td>
<td>ferrimagnetic</td>
</tr>
<tr>
<td>Curie temperature (K)</td>
<td>850</td>
</tr>
<tr>
<td>Std. free energy of formation (kJ mol⁻¹)</td>
<td>–1012.6</td>
</tr>
<tr>
<td>Solubility product (pFe + 3 pOH)</td>
<td>35.7</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1583–1597</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>2623</td>
</tr>
<tr>
<td>Heat of fusion (kJ mol⁻¹)</td>
<td>138.16</td>
</tr>
<tr>
<td>Heat of decomposition (kJ mol⁻¹)</td>
<td>605.0</td>
</tr>
<tr>
<td>Heat of vaporization (kJ mol⁻¹)</td>
<td>298</td>
</tr>
</tbody>
</table>

KONA Powder and Particle Journal
Table 2  General properties of magnetite.

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk magnetite</td>
<td>8.39</td>
<td>590.6</td>
</tr>
<tr>
<td>6.4 nm magnetite</td>
<td>8.40</td>
<td>592.7</td>
</tr>
</tbody>
</table>

2.2 Nano-sized properties

The effective surface area of magnetite particles should increase with decreasing particle size. The effective surface area of 0.2 μm-magnetite particles is approximately 6 m² g⁻¹ and increases considerably to 100 m² g⁻¹ when the size is down to ~50 nm. The change in surface area due to the change in size does not change the crystal structure of magnetite (Li Q. et al., 2017). Nano-sized magnetite still exhibits black color, having a face-centered cubic unit cell of the same lattice parameter and unit cell volume, as shown in Table 2 (Cornell R.M. and Schwertmann U., 2003; Thapa D. et al., 2004).

As discussed above, bulk magnetite is ferrimagnetic at room temperature and has a Curie temperature of 850 K. The magnetic property changes with the change of particle size. The ferrimagnetic behavior of magnetite tends to change towards paramagnetic or superparamagnetic behavior when the particle size is below 6 nm. Superparamagnetic behavior is indicated by a zero remanence and a negligible coercivity in the absence of an external magnetic field. In the size range of 1 to 10 nm, each particle becomes a single magnetic domain, and the energy barrier for its spin reversal is easily overcome by thermal vibrations (Iglesias O. and Labarta A., 2004). Coercivity builds slowly as the particle size increases (Thapa D. et al., 2004).

3. Electrochemical synthesis of magnetite nanoparticles

An electrochemical synthesis is primarily conducted by passing an electric current through two or more electrodes, which consist of an anode and a cathode, in an electrolyte solution. The production of nanoparticles using this method involves the reduction and oxidation (redox) reactions at electrodes that induce precipitation from the solution phase. The reduction process is a reaction where a species in solution accepts an electron from the cathode, and the oxidation process is a reaction where a species in solution releases an electron to the anode. Thus, the redox process is a chemical phenomenon associated with charge transfer to or from an electrode. The amount of electron transfer at the cathode and the anode must be equal.

Electrode reactions are heterogeneous and occur in the interfacial region between electrode and solution. The reactions produce a slight unbalance in the electric charges of the electrode and the solution. Hence, the electrode reactions can be controlled by manipulating the interfacial potential difference through the potential difference between pairs of electrodes in an electrochemical cell.

The kinetic limitation in an electrochemical system at low temperature can be easily overcome by an applied potential or electric field (Bard J.B. and Faulkner L.R., 2001). Therefore, this method can be conducted at a low temperature below the boiling point of the electrolyte. The electrochemical reaction is also sensitive to the characteristics of the electrode surface and the electrolyte composition. The method represents a means of obtaining products that are not possible to gain from conventional chemical synthesis (Fajaroh F. et al., 2012).

3.1 Operation mode

A typical electrochemical cell is illustrated in Fig. 1, which consists of an anode, a cathode, and an electrolyte. During the electrosynthesis, the electrode reactions induce precipitation from the solution phase. Therefore, it appears that the key factors to control the reactions are the applied current and the applied potential. Table 3 presents selected studies on synthesis of magnetite nanoparticles by the electrochemical method. For most studies, the electrochemical synthesis of magnetite nanoparticles is mostly performed under galvanostatic or potentiostatic mode although other modes such as cyclic voltammetry, pulsed potential, and pulsed current are also used. The magnetite nanoparticles produced by the electrochemical method are mainly spherical, although other morphologies, such as nanorod and cubic, can also be produced.

In the galvanostatic mode, the current is controlled to remain constant during the electrosynthesis. Since current is related to the number of materials reacted, it implies...
Table 3  Selected studies on synthesis of magnetite nanoparticles by electrochemical method.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Operation mode</th>
<th>Time</th>
<th>Particle size (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe anode + Fe(ClO$_4$)$_2$</td>
<td>Fe sheet for both anode and cathode</td>
<td>0.01–1 M Fe(ClO$_4$)$_2$ (aq)</td>
<td>Galvanostat: 40–60 mA cm$^{-2}$</td>
<td>30 and 45 min</td>
<td>15–35 (cubic)</td>
<td>(Gopi D. et al., 2016)</td>
</tr>
<tr>
<td>Fe anode</td>
<td>Carbon steel plates for both anode and cathode</td>
<td>0.04 M NaCl (aq) bubbled with air</td>
<td>Galvanostat: 62.5 and 125 mA cm$^{-2}$</td>
<td>20 and 30 min (room temp. and 70 °C)</td>
<td>30.5–45.2 (spherical)</td>
<td>(Weng, Y.C. et al., 2005)</td>
</tr>
<tr>
<td>Fe anode</td>
<td>Fe sheet for both anode and cathode</td>
<td>0.04 M Mg$_2$NCl$_2$ (aq)</td>
<td>Potentiostat: 1–15 V; Galvanostat: 10–200 mA cm$^{-2}$</td>
<td>1800 s (60 °C)</td>
<td>23–33 (spherical)</td>
<td>(Cabrera L. et al., 2008)</td>
</tr>
<tr>
<td>Fe(NO$_3$)$_3$</td>
<td>Three electrodes: carbon disk (WE), Ag/AgCl (RE), Pt rod (CE)</td>
<td>0.01–0.16 M Fe(NO$_3$)$_3$·9H$_2$O in ethanol</td>
<td>Cyclic voltammetry (potential 20–60 V; current 30 mA cm$^{-2}$)</td>
<td>NA</td>
<td>6.2 (spherical)</td>
<td>(Ibrahim M. et al., 2009)</td>
</tr>
<tr>
<td>Fe anode</td>
<td>Three electrodes: Stainless steel pellets (WE), SCE (RE), Pt wire (CE)</td>
<td>0.04 M NaCl; 0.02 M NaSO$_4$; 0.02 M NaSCN; Dissolved in water at pH 10</td>
<td>Galvanostat</td>
<td>30 min</td>
<td>45–80 (spherical)</td>
<td>(Franger S. et al., 2004)</td>
</tr>
<tr>
<td>Fe anode</td>
<td>Fe sheet for both anode and cathode</td>
<td>0.25 M Na$_2$SO$_4$ and 0.04 M stabilizing agent (TU, PA, BU, HMTA, β-CD, or TBA$^{(a)}$)</td>
<td>Potentiostat 5 V (60 °C)</td>
<td>30 min</td>
<td>25–90 (primary); β-CD: agglomerate, fusiform structures; TBA: sheet-like;</td>
<td>(Mosivand S. et al., 2013)</td>
</tr>
<tr>
<td>Fe anode</td>
<td>Three electrodes: Fe foil (WE &amp; CE), SSE (RE)</td>
<td>0.5 M KCl (aq)</td>
<td>Pulsed potential</td>
<td>60 min</td>
<td>27–32 (spherical)</td>
<td>(Rodriguez-López A. et al., 2012)</td>
</tr>
<tr>
<td>Fe anode</td>
<td>Fe sheet for both anode and cathode</td>
<td>2 M KOH with CTAB</td>
<td>Pulsed current ($\lambda = 18$ mA cm$^{-2}$; $f = 8$ Hz)</td>
<td>~67</td>
<td>25–30 (nanorods)</td>
<td>(Karami H. and Chidar E., 2012)</td>
</tr>
<tr>
<td>Fe anode</td>
<td>Fe plate for both anode and cathode</td>
<td>Deionized water</td>
<td>Galvanostat 205–415 μA cm$^{-2}$</td>
<td>20 h</td>
<td>10–30 (spherical)</td>
<td>(Fajaroh F. et al., 2012)</td>
</tr>
<tr>
<td>Fe(NO$_3$)$_3$</td>
<td>Carbon cylinders (anode and cathode)</td>
<td>0.01–0.016 M Fe(NO$_3$)$_3$·9H$_2$O in ethanol</td>
<td>Potentiostat 62 V</td>
<td>12 h</td>
<td>4.4–9 (spherical)</td>
<td>(Marques R.F.C et al., 2008)</td>
</tr>
</tbody>
</table>

$^{(a)}$TU = thiourea; PA = propylamine; BU = sodium butanoate; HMTA = hexamethylene-tetra-amine; β-CD = β-cyclodextrine; TBA = tetrabutylammonium bromide.

Thus, if an aqueous solution is electrolyzed, one or both reactions may compete with the electrolysis of the dissolved substances. The reaction depends on the value of the potential standard $E^\circ$ of the substance relative to that of water.

As an illustration, suppose an aqueous NiCl$_2$ solution is electrolyzed using a Pt electrode. For this case, reactions of Eqns. 3 and 4 occur.

$$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}(s) \quad E^\circ = -0.24 \text{ V (anode)} \quad (3)$$

$$2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^- \quad E^\circ = -1.36 \text{ V (cathode)} \quad (4)$$
Comparison of the $E^\circ$ of reactions 1 and 3 and of reactions 2 and 4 would lead us to predict that the oxidation 3 would be favored over that of 1, and the reduction 4 would be favored over that of 2. When NiCl$_2$ is replaced with NaCl, H$_2$ will be generated at the cathode, not Na. At the cathode, reaction 1 will occur, and at the anode, Cl$^-$ → 1/2 Cl$_2(g)$ + e$^-$ ($E^\circ = -1.36$ V). The value of $E^\circ$ for the Na$^+$/Na pair is −2.714 V, and that for the H$_2$/H$_2$O pair is −0.828 V. Because $E^\circ$$_{\text{Na}^+/-\text{Na}}$ is more negative than $E^\circ$$_{\text{H}_2/\text{H}_2\text{O}}$, reduction of Na$^+$ is more difficult than the reduction of water, meaning that the latter will occur. If Cl$^-$ ion is replaced by an anion that is more difficult to oxidize, such as NO$_3^-$ or SO$_4^{2-}$, water will oxidize.

In a galvanostatic operation, a low current density significantly influences the particle size of magnetite nanoparticles (Fajaroh F. et al., 2012). The particles size increases with the increase in current density. Conversely, the current density has no significant effect on the particle size at high current density, i.e., the particle size is constant even if the current density is varied (Cabrera L. et al., 2008). At high current density, the effects of the diffusion rate and the Helmholtz layer can be ignored during the reaction. In contrast, these effects cannot be neglected at low current density. As a result, both charge transfer and diffusion rate have a significant effect on the overall reaction of magnetite formation at low current density, i.e., low reaction rate.

Alternatively, pulsed potential or pulsed current has been used to produce magnetite nanoparticles (Setyawan H. et al., 2014). The use of pulsed potential or pulsed current can effectively prevent the particle aggregation and bubble formation that occur during synthesis due to the electrolysis of water. Particles dispersed in an electrolyte carry electrical charges due to the attachment of ions surrounding the particles. In the presence of the electrical field, especially near the electrode surface, the motion of charged particles is influenced by electrophoretic and electroosmotic forces (Naim M.N. et al., 2010). Hence, the charged particles are accelerated towards the electrode surface and tend to collide with each other to form an aggregate. Under pulsed potential or pulsed current, the motion of particles due to the two forces are stopped at the off-condition that prevents particles collision and, in turn, particles agglomeration (Rodríguez-López A. et al., 2012).

The potentials of the pulses must be appropriately selected to ensure the formation of magnetite. The applied minimum and maximum values of the potential pulses must cover the potential reductions of ferric to ferrous ions, of water to hydroxyl ions and of ferrous ion to metallic iron, and the oxidation of iron to ferric species. Using a disymmetric pattern of potential pulses, i.e., changing the polarity of the electrodes, ferrous and ferric ions are generated when the iron acts as an anode and later generates hydroxyl ions to form chemically ferric hydroxide while simultaneously reducing that hydroxide to magnetite, when it acts as a cathode (Karami H. and Chidar E., 2012). In this way, the energy related to the mass transfer of hydroxyl ions generated at the cathode to the anode can be saved because they are no longer traveling to the other electrode.

The particle morphology can be controlled to become nanorods under pulsed current mode with the addition of surfactant (Karami H. and Chidar E., 2012). The nanorod structures in the pulsed-electrochemical synthesis may be formed as the result of the directional growth of initial magnetite formed on the electrode surface. The pulsed current slows the chemical reaction rate and may influence the nucleation process and growth. The electric field created during the pulsed current may interact with chemical reaction systems since it contains charged ions such as Fe$^{3+}$, Fe$^{2+}$ and OH$^-$ that form Fe$_3$O$_4$ cluster with a structural motif. If the electrostatic force is parallel to or far greater than the composition of forces in the structural motif and the nucleation process and growth are prolonged, structural motifs are likely to follow the minimum energy principle and growth along the easy electric field axis occurs to build single-crystal rod-like structures (Zhang W. et al., 2011).

Based on the above descriptions of various modes of operation to synthesize magnetite nanoparticles by an electrochemical method, the advantages and disadvantages can be understood. The applied potential to the electrochemical cell is constantly controlled using the potentiostat mode. This approach ensures that the electrochemical reactions taking place in the system can be maintained during the synthesis. Using the galvanostatic mode, the current supplied to the cell is set constant. The mode ensures the kinetics of reaction can be maintained over the period of synthesis. The potential may change, however, during the synthesis, influencing the electrochemical reactions in the system. It seems that the potential mode can give the desirable electrochemical reactions. As the precipitation is strongly influenced by the concentration of the reactants, however, the current mode is likely to be a better choice. If it is desired to have monodispersed, uniformly sized, stable magnetite nanoparticles, the pulsed mode may become the most suitable choice, but it requires considerably more time to obtain the desired amount of product.

### 3.2 Precursors and electrolytes

The most common method to prepare magnetite nanoparticles by electrochemical synthesis is electro-oxidation of iron (see Table 3). Typically, the iron source acts as an anode in an electrochemical cell. When the current/voltage is imposed on the cell, the iron is oxidized to become Fe$^{3+}$ ions that are dissolved in the electrolyte solution. The
The presence of Mg$^{2+}$ ions subsequently interact with other ions to form iron oxide nanoparticles, either in the anode or cathode regions. In this case, the particles are generated by a primary nucleation and growth process. The continuous supply of Fe$^{2+}$ ions generated by anodic dissolution causes a high concentration of Fe$^{2+}$ ions, and when the concentration reaches supersaturation, homogeneous nucleation begins. The nuclei start colliding with each other and coagulation occurs to form larger particles.

The formation of magnetite nanoparticles using the sacrificial iron anode is influenced by certain parameters, the most critical one is the distance between electrodes. If the distance between electrodes is far away, the region close to anode will not reach a pH value necessary to form iron hydroxide. Although the hydroxide ion is formed, it would not reduce at the cathode, at least not in an appreciable amount. Thus, there is a critical distance at which magnetite nanoparticles can be formed (Fajjaroh F. et al., 2012). It is apparent that pH is also a critical factor in the formation of magnetite nanoparticles. The formation of magnetite is favored in basic condition, typically at a pH between 9 and 11 (Ramimoghadam D. et al., 2014).

The supporting electrolyte solution is often necessary to enhance the electrical conductivity of solution during the electrochemical synthesis. The electrolyte must be appropriately selected for the magnetite nanoparticles to be formed. For example, magnetite can be formed in NaCl solution in the presence of Mg$^{2+}$ and Ca$^{2+}$ ions, while it is formed only slightly in the presence of Cu$^{2+}$ ions (Ying TY. et al., 2002). The presence of Mg$^{2+}$ and Ca$^{2+}$ ions hinders the formation of magnetite particles because both ions tend to precipitate or incorporate in the particles. This problem can be overcome, however, by adding a strong electrolyte such as NaCl that significantly increases the conductivity and, in turn, increases the current density. On the other hand, the presence of Cu$^{2+}$ ions interfere with the formation of magnetite particles. In this case, the Cu$^{2+}$ ions make the pH of the solution lower due to the formation of Cu$_2$O. When Cu$_2$O is formed, hydrogen ions are produced, decreasing the pH, which leads to unfavorable condition for magnetite formation.

In addition to enhancing the conductivity, the electrolyte may also act as a surfactant or complexing agent. For example, amines are surfactants that acts as a supporting electrolyte and coating agent to control particle size and aggregation during synthesis (Cabrera L. et al., 2008). The magnetite nanoparticles produced using this surfactant have sizes between 20 and 30 nm. Various compounds may be used to serve as a complexing or stabilizing agent such as salts, e.g., NaCl, Na$_2$SO$_4$, NaSCN and Na$_2$S$_2$O$_3$ (Franger S. et al., 2004) and organics, e.g., thiourea, propylamine, sodium butanoate, hexamethylene-tetra-amine, β-cyclodextrin and tetrabutylammonium bromide (Mosivand S. et al., 2013), and CH$_3$H$_2$NCl (Cabrera L. et al., 2008).

The role of the complexing entities in the electrolytes is the most critical one is the distance between electrodes. If the distance between electrodes is far away, the region close to anode will not reach a pH value necessary to form iron hydroxide. Although the hydroxide ion is formed, it would not reduce at the cathode, at least not in an appreciable amount. Thus, there is a critical distance at which magnetite nanoparticles can be formed (Fajjaroh F. et al., 2012). It is apparent that pH is also a critical factor in the formation of magnetite nanoparticles. The formation of magnetite is favored in basic condition, typically at a pH between 9 and 11 (Ramimoghadam D. et al., 2014).

Combining an iron anode precursor and an aqueous solution of Fe(ClO$_4$)$_2$ to produce magnetite nanoparticles by the electrochemical method changes the particle morphology from spherical to cubic (Gopi D. et al., 2016) giving particle size was in the range of 15 to 35 nm. Another precursor to synthesize magnetite nanoparticles by the electrochemical method is Fe(NO$_3$)$_3$ in ethanol medium (Ibrahim M. et al., 2009; Marques R.F.C. et al., 2008). The magnetite nanoparticles produced using this precursor have sizes ranging from 4.4 to 9 nm. The purity of the product is quite vulnerable to the iron concentration and current density. Moreover, this method requires a relatively water-free bath to obtain pure magnetite nanoparticles. The presence of water tends to favor the formation of Fe(OH)$_2$, which contaminates the magnetite nanoparticles.

It is well-known that the chemical co-precipitation method of iron salts is the most common technique to produce magnetite nanoparticles. This method is a straightforward and efficient wet chemical route. Magnetite is precipitated from an aqueous solution of Fe(II) and/or Fe(III) salts with alkali along with suitable aging time. The reaction in this system is very fast, making it difficult to control the precipitation process, and in turn, monodispersed nanoparticles are difficult to obtain. Since the precipitation is mainly governed by adjusting the solution pH by adding OH$^-$, this ion can be supplied with well-controlled rate by water reduction in an aqueous electrochemical cell (Aghazadeh M. et al., 2017; Karimzadeh I. et al., 2017a). It can be performed by electrolyzing an aqueous solution of Fe(II) and Fe(III) with a molar ratio of 1:2 using a stainless steel cathode and graphite anode. During the electrolysis, OH$^-$ ions are produced by water reduction at the cathode (Eqn. 2). The OH$^-$ ions later induce magnetite formation through the chemical reaction:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (5)$$

As in the conventional co-precipitation method, when the Fe$^{3+}$/Fe$^{2+}$ ratio is 2:1, magnetite can be generated when the pH is in the range of 8 to 14 (Franger S. et al., 2004; Manrique-Julio J. et al., 2016; Melnig V. and Ursu L., 2011).
3.3 Mechanism of particle formation

There are several different proposed mechanisms for the electrochemical formation of magnetite nanoparticles. The proposed mechanisms have been compiled and discussed thoroughly by Lozano I. et al. (2017). In general, the proposed mechanisms can be divided into four groups although the detail steps for each group may be different. They are (i) iron hydroxide reduction at the cathode (Cabrera L. et al., 2008; Ibrahim M. et al., 2009; Rodríguez-López A. et al., 2012; Ying T.Y. et al., 2002), (ii) hydrogen gas as a reducing agent of iron hydroxide (Franger S. et al., 2004; Manrique-Julio J. et al., 2016; Melnig V. and Ursu L., 2011), (iii) direct reaction between Fe$^{2+}$ and Fe$^{3+}$ (Karami H. and Chidar E., 2012; Ying T.Y. et al., 2002), and (iv) oxygen as oxidant agent and subsequent in-solution precipitation (Fajaroh F. et al., 2012; Gopi D. et al., 2016; Lozano I. et al., 2017; Pascal C. et al., 1999; Starowicz M. et al., 2011).

The first step for all of the proposed mechanisms involves the production of Fe$^{2+}$ ions by the oxidation of a sacrificial iron anode and OH$^-$ ions by the reduction of water at the cathode. The iron oxidation at the anode and water reduction at the cathode can be written, respectively, as

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (6)$$
$$\text{H}_2\text{O} + e^- \rightarrow 1/2 \text{H}_2 + \text{OH}^- \quad (7)$$

The subsequent mechanism steps are different for the four proposed mechanisms as will be discussed in the following. In the first and second mechanisms, Fe$^{2+}$ ions are further oxidized to Fe$^{3+}$ and in the presence of an OH$^-$ ions leads to the formation of Fe(OH)$_3$. The Fe$^{3+}$ ion is later reduced at the cathode to produce Fe$_3$O$_4$. The difference between the two mechanisms is the reducing agent. The reduction of the first mechanism occurs on the cathode surface via Faradaic reaction (Eqn. 8) and the second one by hydrogen produced on the cathode (Eqn. 9).

$$3\gamma\text{FeOOH}(s) + e^- \rightarrow \text{Fe}_3\text{O}_4(s) + \text{H}_2\text{O} + \text{OH}^- \quad (8)$$
$$3\gamma\text{FeOOH}(s) + 1/2 \text{H}_2 \rightarrow \text{Fe}_3\text{O}_4(s) + 2\text{H}_2\text{O} \quad (9)$$

As noted by Lozano I. et al. (2017), however, it is unlikely that solid species such as Fe(OH)$_3$ can reach the cathode to undergo reduction. Additionally, due to its high propensity to escape from the reacting medium, it is almost impossible for hydrogen gas to react with iron hydroxide (Eqn. 9).

In the direct reaction mechanism, in addition to Fe$^{2+}$ ions, Fe$^{3+}$ ions are also produced on the anode surface. The two ions then react to form Fe$_3$O$_4$ in the presence of OH$^-$ ions following the reaction

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O} \quad (10)$$

This mechanism has, however, a lack of further explanation.

The last mechanism which involves dissolved oxygen as an oxidizing agent for Fe(OH)$_3$ in solution to produce magnetite seems to be the most likely appropriate to describe the electrochemical formation of magnetite nanoparticles. This mechanism was first proposed by Fajaroh F. et al. (2012), and the validity was confirmed by Lozano I. et al. (2017) through experimental strategies to provide relevant information to prove the mechanisms. In brief, Fe$^{2+}$ ions produced by iron dissolution (Eqn. 6) in the presence of OH$^-$ ions precipitate to Fe(OH)$_3$. In the presence of oxygen, Fe(OH)$_3$ can be partially oxidized to form FeOOH, and they transform into magnetite when an appropriate proportion of the two substances is achieved. They can be summarized as, after Eqns. 6 and 7,

$$3\text{Fe(OH)}_2 + 1/2 \text{O}_2 \rightarrow \text{Fe(OH)}_3 + 2\text{FeOOH} + \text{H}_2\text{O} \quad (11)$$
$$\text{Fe(OH)}_3 + 2\text{FeOOH} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \quad (12)$$

Reaction 11 represents partial oxidation of ferrous hydroxide in the presence of oxygen to form FeOOH. Magnetite is formed when an appropriate proportion of Fe(OH)$_3$ and FeOOH is created by reaction 12.

4. Electrochemical synthesis of functional magnetite nanoparticles

The magnetite nanoparticles may be modified at their surface to have functional properties and applications. These functional nanoparticles are also be obtained by the combination of two or more constituents. The surface modification or the combination of more than one material may give rise to many varieties of properties that lead to various applications. For example, bare magnetite nanoparticles are susceptible to degradation in some environments, e.g., dissolve in an acidic environment (Setyawan H. et al., 2012) and susceptible to air oxidation (Fajaroh F. et al., 2013; Setyawan H. et al., 2012; Vatta L.L. et al., 2007). One way to protect magnetite nanoparticles from possible acid dissolution or air oxidation is by coating the particles with a more inert material, such as silica (Fajaroh F. et al., 2013; Setyawan H. et al., 2012). The electrochemical method seems to be effective and efficient to produce functional magnetite nanoparticles.

When an electrochemical route using a sacrificial iron anode coupled with an appropriate electrolyte, two metal oxide nanoparticles may be produced. For example, nickel ferrite (NiFe$_2$O$_4$) nanoparticles can be produced using two sheets of iron and nickel as sacrificial anodes in a three-electrode electrochemical cell (Galindo R. et al.,...
Cobalt ferrite (CoFe$_2$O$_4$) nanoparticles having a size of approximately 20 nm are produced when the nickel sheet is replaced by cobalt (Mazario E. et al., 2012, 2013). The nickel ferrite nanoparticles have a cubic spinel structure and are spherical with sizes in the range of 5-45 nm. The same crystal structure and particle shape can be obtained for cobalt ferrite nanoparticles, but with a particle size of approximately 20 nm. Both kinds of ferrite particles have soft ferromagnetic behavior with a saturation magnetization of 48 emu/g (bulk 55 emu/g) and coercivity 31 Oe for nickel ferrite, and 71 emu/g (bulk 80 emu/g) and 442 Oe for cobalt ferrite.

When the electrolyte solution is dilute aqueous sodium silicate, silica-coated magnetite nanoparticles are produced (Setyawan H. et al., 2012). The silica-magnetite nanoparticles produced by this system are spherical, with a mean size ranging from 6 to 10 nm. They exhibit superparamagnetic properties with a saturation magnetization of approximately 20 emu/g. The superparamagnetic behavior of the silica-coated magnetite nanoparticles which is different from that of magnetite nanoparticles synthesized by the same electrochemical approach is probably caused by the smaller size of particles (< 10 nm). For very small particles, the energy barrier for its spin reversal is easily overcome by thermal vibrations because each particle becomes a single magnetic domain (Iglesias O. and Labarta A., 2004). The silica layer formed by this method is stable and can serve as a protective layer against an acidic environment and high temperature (Fajaroh F. et al., 2013; Setyawan H. et al., 2012).

Magnetite nanoparticles coated with polydopamine can be obtained when the electrochemical oxidation of iron is performed in the presence of dopamine (Mazario E. et al., 2014). The polydopamine-coated magnetite nanoparticles are spherical with the size varying between a few nanometers and 25 nm. The polymer coating makes the nanoparticles suitable for use in biomedical applications due to their excellent physicochemical and magnetic properties, excellent biocompatibility and nontoxicity. Polyvinyl alcohol (PVA)-coated magnetite nanoparticles of size 64 nm can also be obtained by electrodeposition using an iron chloride/nitrate solution in the presence of PVA (Karimzadeh I. et al., 2017a). Other organics such as vitamin C and sucrose have also been successfully used to coat magnetite nanoparticles by electrodeposition (Aghazadeh M. et al., 2017).

It appears that the electrochemical method is an efficient and facile route to synthesize functional magnetite nanoparticles. The substitution of iron in the magnetite or coating magnetite nanoparticles can be performed in one single step by merely changing the electrode or electrolyte composition.

5. Scale-up

As discussed above, the electrochemical cell can be scaled up easily by enlarging the current density/potential and electrode size. The electrochemical cell used for the production of magnetite nanoparticles discussed above primarily consists of two electrodes, with one acting as the sacrificial anode for the iron precursor. The production rate of nanoparticles using such an electrode arrangement is very lacking in quantity. At a current density of 0.3 mA/cm$^2$, it takes 20 h to produce approximately 0.7 g of magnetite nanoparticles. The production rate can be increased significantly by enlarging the electrode size with the same reactor volume using many electrodes with the monopolar arrangement as shown in Fig. 2, in which each electrode is connected individually (Manrique-Julio J. et al., 2016).

6. Summary

The methods for the preparation of magnetite nanoparticles by electrochemical technique are briefly reviewed. The electrochemical method has emerged as an option for the preparation of magnetite nanoparticles and their composites. This method offers many advantages over other techniques. One advantage is that this method can easily control particle size by adjusting the imposed current and potential to the system. Additionally, the system is scalable to mass production by merely increasing the current or potential and enlarging the size of the electrode.

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