Synthesis and Characterization of $\alpha$-$\text{Fe}_2\text{O}_3$ Nanoparticles by Microemulsion Method

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Abstract

In this study, $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles (NPs) were synthesized by microemulsion method. Synthesized NPs were characterized by X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectra, and UV-Visible techniques. According to TGA analysis, it has been observed that a complete formation of Fe$_2$O$_3$ at around 400 °C. According to SEM images, plate like structure formation was observed in $\alpha$-$\text{Fe}_2\text{O}_3$ NPs with homogeneous dispersion. Approximately 13.1 nm particle size was calculated from the XRD data by using the Scherrer equation. Fe-O vibrations in octahedral and tetrahedral regions were obtained in the FTIR spectrum. According to UV-Vis spectrum, it was determined that NPs showed optical absorption feature at wavelength of around 420 nm. In addition, optical band gap of the $\alpha$-$\text{Fe}_2\text{O}_3$ NPs was calculated 3.2 eV.

Keywords: $\alpha$-$\text{Fe}_2\text{O}_3$, microemulsion method, nanoparticle

1. Introduction

Nanomaterials with unique physical and chemical properties are synthesized using a variety of methods such as chemical reduction, photochemical reduction, electrodeposition, coprecipitation, spray-pyrolysis, hydrothermal, and sol-gel. In recent years, the microemulsion method has been extensively investigated for the synthesis of...
nanomaterials as a method versatile, narrow size distribution, good dispersibility and repeatable method that gives control over the nanoparticle size (Pournajaf and Tabrizi, 2015; Pournajaf et al., 2014; Laokul et al., 2015; Chen et al., 2015a; Najjar et al., 2014, Chen et al., 2015b). Monodisperse nanoparticles can be prepared using simple apparatus at room conditions of temperature and pressure with the microemulsion method. So, the microemulsion method has been considered as an ideal method for synthesis inorganic materials (Sarkar et al. 2011; Han et al. 2015). Microemulsions are thermodynamically and isotropically stable dispersions consisting of at least three components as apolar phase (usually water), polar phase (usually oil) and surfactant (Pournajaf et al., 2014; Laokul et al.,2015; Sarkar et al. 2011). Microemulsions are two types as oil-in-water (O/W) or direct microemulsion method and water-in-oil (W/O) or reverse microemulsion method and the second compound is the dispersion medium or solvent. It is remarkable because of the water-in-oil / reverse microemulsion offers nanoparticle synthesis with narrow size distribution and controllable particle size (Shojaei et al., 2014; Foroughi et al., 2015; Strom et al., 2018). Thermodynamically stable dispersions, called reverse micelles, are composed of a continuous oil phase and a dispersed water droplet phase can be considered as true nanoreactors that can be used specifically to synthesize inorganic nanomaterials (Ye et al., 2018). In addition, reverse microemulsions exhibit self-assembly behaviour and this situation is very important for the synthesis of nanomaterials (Lai et al., 2019).

Surfactant molecules adsorb in interfaces and they reduce the interfacial tension and free energy. They are used to stabilize microemulsions by preventing the aggregation of nanoparticles (Sarkar et al., 2011; Shiri et al. 2019). Sodium bis (2-ethylhexyl) sulfosuccinate (AOT), which is an anionic surfactant, can self-assemble into the reverse cylindrical and spherical micelles in various solvents. AOT is one of the surfactants commonly used in water-in-oil microemulsion systems (Lai et al., 2019; Shiri et al., 2019). By controlling the parameters of the microemulsion method, nanoparticles with different size and morphology can be obtained. These parameters are a) reactants concentration and type, b) process parameters such as pH, temperature, stirring method and time (Beygi and Babakhani, 2017). The two water-soluble reactants are dissolved separately in two microemulsions. The resulting microemulsions are then mixed together and they provide the precipitation reaction to form in the aqueous core of the reverse micelles to form nanoparticles (Han et al., 2015).

Iron oxide (Fe$_2$O$_3$) nanoparticle is an important metal oxide widely used in many fields such as catalysts (Koukabi et al., 2011), coatings (Lu et al., 2020), sensors (Wang et al., 2020), photocatalytic systems (Xiang et al., 2020) and drug delivery (Khokhlova 2016). Fe$_2$O$_3$ has four polymorphs consisting of $\alpha$-Fe$_2$O$_3$, $\beta$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$ and $\varepsilon$-Fe$_2$O$_3$. Each polymorph has its specific crystal structure and physical properties. $\alpha$-Fe$_2$O$_3$ (hematite) is important among these polymorphs due to synthesis low toxicity, abundance, environmentally friendly nature, low cost, easy production and storage, high corrosion resistance, chemical inertness, biocompatibility and excellent substrate adhesion (Mirzaei et al., 2016). In addition, it is used in many areas mentioned above.
In this study, α-Fe$_2$O$_3$ nanoparticles (NPs) were synthesized with microemulsion method. Thermal, morphological, crystal structure and spectroscopic properties of the NPs were investigated. In addition, the optical absorption spectrum of the α-Fe$_2$O$_3$ NP, and their optical absorption feature was investigated. Optical band gap of the α-Fe$_2$O$_3$ NPs was calculated by using Tauc Equation.

2. Material and Methods

2.1. Materials

Iron (III) chloride (FeCl$_3$) obtained from Merck company was used as precursors. The surfactant dioctyl sulfosuccinate sodium salt (AOT), 1-butanol, n-heptane and sodium hydroxide (NaOH) were purchased from Sigma–Aldrich Company in analytical grade. All experiments were performed by using deionized water.

2.2. Synthesis of nanoparticles

α-Fe$_2$O$_3$ nanoparticles (NPs) were synthesized by water-in-oil (W/O) microemulsion composed of n-heptane as oil phase, anionic surfactant of AOT, co-surfactant of 1-butanol and precipitation agent as NaOH (Han et al., 2015; Khalili and Tabrizi, 2017). The selected W [(H$_2$O)/(AOT)] in molar ratio] value was 8.

Two types microemulsion systems were prepared as microemulsion 1 and microemulsion 2. Firstly, a microemulsion solution prepared by dissolving AOT in 45 mL n-heptane and 5 mL 1-butanol. Then, microemulsion 1 was prepared by mixing the suitable amount of 0.58 M NaOH aqueous solution into the microemulsion solution. In the next system, suitable amount of 0.58 M FeCl$_3$ aqueous solution was mixed with a separate microemulsion solution to obtain the microemulsion 2 solution. Then, microemulsion 1 was added dropwise to microemulsion 2 and they were stirred for 1 h to form a precipitate. The mixture was filtered, washed with acetone and distilled water and then dried at room temperature. The sample were calcined at 500 °C for 2 h in the air atmosphere.

2.3. Characterization

Morphological properties of the NPs were determined by using Scanning Electron Microscope (SEM, Zeiss Sigma 300). X-ray diffraction (XRD) patterns were obtained using PANalytical Empyrean Instrument. Surface functional groups of the NPs were determined by using Fourier-transform infrared spectroscopy (FTIR, Bruker VERTEX 70v). Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) were studied in a Perkin Elmer STA 8000 in air atmosphere. The optical transmission/absorption spectra of the particles in deionized water were recorded using a Shimadzu UV-3600 Plus spectrometer.

3. Results and Discussion

Fig. 1 shows the TGA, DTG and DSC results. The weight loss observed in between 25 and 180 °C can be attributed to the removal of water. The chemical reactions during Fe$_2$O$_3$ formation are believed to be as following (Waseem et al., 2013):

\[
\begin{align*}
2\text{Fe(OH)}_3 & \rightarrow 2\text{Fe}_{0.5}\text{(OH)}_2 + \text{H}_2\text{O} \\
2\text{Fe}_{0.5}\text{(OH)}_2 & \rightarrow 2\text{FeO(OH)} + 2\text{H}_2\text{O} \\
2\text{FeO(OH)} & \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}
\end{align*}
\]
Synthesis and Characterization of $\alpha$-Fe$_2$O$_3$ Nanoparticles by Microemulsion Method

**Figure 1.** TGA, DTG and DSC results of uncalcined sample

It has been observed that a complete conversion of Fe(OH)$_3$ to Fe$_2$O$_3$ up to 350 °C does not occur and still preserves several OH groups. According to DTG and DSC profiles, it has been observed two peaks associated with exothermic reactions at around 250 and 350 °C. These peaks are related to the transformation of amorphous phase to crystalline Fe$_2$O$_3$ and its transformation to $\alpha$-Fe$_2$O$_3$, respectively (Waseem et al., 2013; Mirzaei et al., 2016).

According to XRD results in Fig. 2, characteristic diffraction peaks at 2$\theta$ values of 24.2°, 33.2°, 35.7°, 41.1°, 49.5°, 54°, 57.3°, 62.4°, and 64° correspond to the (012), (104), (110), (113), (024), (116), (018), (214), and (300) planes of hexagonal $\alpha$-Fe$_2$O$_3$ were observed. The results indicated that the product are consisted of pure phases (Lin and Liaw 2015; Zainuri 2017; Kamali et al., 2014; Li et al., 2016). The particle size of the prepared Fe$_2$O$_3$ nanoparticles were calculated from the XRD data using the following equation (i.e., Scherrer equation): (Patterson 1939).

$$D = \frac{K \cdot \lambda}{B \cdot \cos \theta_B}$$

where $D$ is average particle size, $K$ is the Scherrer constant ($K=0.9$), $\lambda$ is the wavelength of radiation ($\lambda_{Cu,K\alpha}=0.154$ nm), and $B$ is the integral breadth of peak (in radians 20) located at angle $\theta_B$.

The (104) plane was selected to calculate the particle size $\alpha$-Fe$_2$O$_3$. It was found that the particle size of Fe$_2$O$_3$ is about 13.1 nm. A particle size lower than that given in the literature was obtained (Kamali et al., 2014; Mirzaei et al., 2016; Li et al., 2016).

**Figure 2.** XRD pattern of $\alpha$-Fe$_2$O$_3$

According to FTIR spectra in Fig. 3, the bands at 1130, 560 and 440 cm$^{-1}$ correspond to characteristic features of $\alpha$-Fe$_2$O$_3$ and these peaks represent the metal oxygen stretching vibrational modes. The high frequency band at 560 cm$^{-1}$ can be attributed to Fe-O deformation in the octahedral and tetrahedral regions, while the low frequency band at 440 cm$^{-1}$ can be related to the Fe-O deformation in the octahedral region of hematite (Mirzaei et al., 2016; Li et al., 2016).
Figure 3. FTIR spectrum of α-Fe₂O₃

The SEM images of the NPs are given in Fig. 4. Plate like structure formation was observed in α-Fe₂O₃ NPs with homogeneous dispersion.

Figure 4. SEM images a) 5.00 KX Mag b) 50.00 KX Mag for α-Fe₂O₃

Figure 5 shows the optical absorption spectrum of the α-Fe₂O₃ NPs, and the optical absorption feature was observed at wavelength between 380-540 nm. The peak between 380-400 nm and the shoulder at 540 nm are originate from indirect Fe 3d to 3d and direct O 2p to Fe 3d transitions (Taffa et al., 2015).

Figure 5. UV-Vis spectrum of α-Fe₂O₃

In order to determine the optical band gap value of α-Fe₂O₃ NPs, the optical data have been calculated by using Tauc Equation (4) (Tauc 1970).

\[ \alpha h\nu^2 = A (h\nu-E_g)^n \]  

(4)

where, the exponent n is a constant depending on the kind of optical transition, A is an effective mass constant, h\nu is the energy of photons and E_g is the optical band gap. Owing to the indirect band transition in α-Fe₂O₃, the value of n was taken as 2 (Kuhaili et al., 2012; Silva et al., 2013).

As shown in Fig.6, the optical band gap of the α-Fe₂O₃ is 3.2 eV and it has an inflection and shift to the red wavelength compared to that reported by Yoon et al. and Taffa et al. (Yoon et al., 2014; Taffa et al., 2015).
4. Conclusion

In this study, α-Fe₂O₃ NPs were synthesized by microemulsion method. The NPs showed the plate-like morphology. According to the XRD result, the formation of α-Fe₂O₃ NPs was observed. The crystallite size of the prepared α-Fe₂O₃ NPs was about 13.1 nm. According to FTIR spectrum peaks of characteristic properties of α-Fe₂O₃ were observed. In addition, TGA, DSC and DTG peaks are related to the transformation of amorphous phase to crystalline Fe₂O₃ and its transformation to α-Fe₂O₃, respectively. Optical band gap of the obtained α-Fe₂O₃ NPs was found as 3.2 eV. Compared to the literature, α-Fe₂O₃ NPs with a quite low particle size were obtained using the microemulsion method. Therefore, the microemulsion method is a very important method for the synthesis of nanoparticles.

5. References

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Synthesis and Characterization of α-Fe$_2$O$_3$ Nanoparticles by Microemulsion Method

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