Effect of Annealing Temperature on the Crystal and Morphological sizes of Fe$_2$O$_3$/SiO$_2$ Nanocomposites

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Abstract. Annealing the synthesized materials at different temperatures is very significant in ensuring the complete removal of the impurities during the particle formation process. Recently, nanocomposites material has shown reasonable outcomes and performed exclusively over bare single nanoparticles (NPs) in various fields of studies. In this paper, the composite of Fe$_2$O$_3$/SiO$_2$ nanomaterial was synthesized via a Sol-gel auto-combustion method with aid of organic precursors. The material was synthesized at various concentrations and annealed at different temperatures. Characterization of the composite material was done by analyzing crystal structures, elemental composite distributions, morphologies, and chemical compositions via X-Ray Diffraction (XRD), Energy dispersed X-ray (EDX), Field Emission Scanning Electron Microscopy (FESEM), and Fourier-Transform Infrared Spectroscopy (FTIR), respectively. The chemical interaction between amorphous silica and iron oxide nanoparticles has been established due to the manifestation of the characteristic wavelengths corresponding to the linkage bond between the amorphous silica and iron oxide nanoparticles. The FESEM imaging revealed that the morphological size increased significantly with an increase in temperature. Furthermore, in the XRD experiment, it was found that increasing the temperature has significantly improved the crystal properties of the composite material. Hence, annealing temperature can serve as a reliable method that can control the morphological size and crystal structure of the materials.

1. Introduction
Nanotechnology is identified among the new fields of science and technology that is extensively studied and displayed promising results in modern science and technology [1]. Nanocomposites material is a combination of two or more different nanoparticles with distinct chemical or physical characteristics. The subsequent composite exhibits properties which are unique and hopefully better and superior to the single nanomaterial. According to Okpala et al. [2], nanocomposite materials have rapidly propelled by displaying positive, exclusive, and better performance in various fields. Recently, metal oxide nanoparticles have shown promising results in various fields and performed reasonably [3]. Silica-based nanoparticles are widely and extensively used in various applications because their physical and chemical properties can easily be manipulated, which makes them applicable in numerous fields [1]. Hence, combining these two nanoparticles is expected to offer a promising means in various applications better than an individual or single nanomaterial. It was reported that combining silicon dioxide with different metal oxides such as TiO$_2$ and Fe$_2$O$_3$ nanoparticles display significant properties for various applications [4]. Moreover, when silica is embedded on the surface of metal oxide NPs, good stability
will be achieved, and the effect of free radicals during photocatalysis will eventually reduce, and flexibility of the surface modification could equally achieved [5]. The Fe$_2$O$_3$/SiO$_2$ composite materials were firstly studied in 1981 by Yoshila et al. [6].

Subsequently, the composite of Fe$_2$O$_3$/SiO$_2$ was extensively used in medical applications most importantly in cancer treatment because of its magnetic properties capable of generating and transmitting heat for the treatment of tumor tissues [7]. The Fe$_2$O$_3$/SiO$_2$ could also be used in infrared imaging and magnetic resonance imaging for cancer treatments [8]. Apart from the medical application, this composite material was found to be essential in various applications such as magneto-optical sensors, etc. which is attributed to the high-class performance observed in terms of their physical and chemical properties. When the reaction between Fe$_3$O$_4$ and SiO$_2$ is taking place, the particles of silicon could shade the magnetic dipolar attraction between Fe$_3$O$_4$ particles which demonstrates a uniform dispersion in various fluids. Moreover, the leaching of the magnetic particles is equally tackled by the presence of silica particles [9].

In this paper, the effect of the annealing temperature on the composite material of Fe$_2$O$_3$/SiO$_2$ was investigated concerning its morphological and crystal properties. The composite materials were synthesized via sol-gel methods at various temperatures in different mole ratios. Characterization methods such as XRD, EDX, FESEM, and FTIR were employed to analyze the phase structures and crystal size of the particles, elemental composite distributions, morphologies, and chemical compositions.

2. Materials and Methods

2.1 Materials Preparation

Iron Oxide NPs (Fe$_3$O$_4$), Tetraethyl orthosilicate (TEOS), Ammonia solution (NH$_4$OH), Deionized water, Ethanol (C$_2$H$_6$O).

The Fe$_2$O$_3$/SiO$_2$ was synthesized at different mole ratio (1:1, 2:1 & 1:6). The Fe$_2$O$_3$ NPs powder was dispersed in the mixture containing distilled water (50 ml), and ethanol (250 ml), the solution was further agitated in an Ultrasonic bath for 30 min to ensure longer dispersion of the powder particles in the solution. Thereafter, tetraethyl orthosilicate (TEOS) was added in an ammonia solution (6 ml), and then added to the suspension of the Fe$_2$O$_3$. Glass magnetic stirrer was used to stir the resulting mixture for 5 h. The solid particles were then washed severely and thereafter dried in an oven at 40°C for 24 h, hence the composite powder was formed. Consequently, the synthesized materials were crushed into powder using mortar and pestle and calcined at different temperatures (200, 250, and 300 °C) as described in figure 1. The synthesis procedure was adopted from Ref. [10] with little modification.

Figure 1: Flow chart for the synthesis of Fe$_2$O$_3$/SiO$_2$ nanocomposites
2.2 Characterizations of the synthesized nanocomposites materials
Fe$_2$O$_3$/SiO$_2$ nanocomposites materials were characterized to confirm the structural, physical, and chemical properties. XRD was utilized to determine the crystal structure of the material, FESEM was used to identify the surface morphology of the composite materials, the particle size distribution of the composite materials was analyzed by EDX, and chemical properties of the materials were analyzed by FTIR.

3. Results & Discussion
3.1 Morphological analysis of Fe$_2$O$_3$/SiO$_2$
The surface morphology of Fe$_2$O$_3$/SiO$_2$ observed using FESEM is shown in Figure 3. The average morphological size annealed at different temperatures has shown no significant difference in the shape distribution of the particles. However, the average morphological size was significantly increased with an increase in temperature in such a way that the particle size was observed to increase from 37 to 64 due to increasing temperature as shown in table 1. It can also be observed that the particles of Fe$_2$O$_3$ and SiO$_2$ that formed composite are highly agglomerated with an irregular pattern which was due to the successful accomplishment of the hydrolysis of the sol-gel precursor. Furthermore, this was also attributed to the strong attraction between molecules of iron oxide NPs and that of silica NPs [10].

![Figure 3: FESEM Images of Fe$_2$O$_3$/SiO$_2$ a) ambient temp. b) 200 °C (C) 250 °C (d) 300 °C](image-url)
### Table 1: Particle size of Fe₂O₃/SiO₂ nanocomposites at different temperatures

| Samples                   | Average particle size (nm) |
|---------------------------|----------------------------|
| Fe₂O₃/SiO₂ @ ambient temp. | 37                         |
| Fe₂O₃/SiO₂ @ 200 °C       | 56                         |
| Fe₂O₃/SiO₂ @ 250 °C       | 58                         |
| Fe₂O₃/SiO₂ @ 300 °C       | 64                         |

### 3.2 Energy dispersed X-ray (EDX) analysis of Fe₂O₃/SiO₂

The elemental distribution in the synthesized composite materials of Fe₂O₃/SiO₂ has been observed as shown in Figures 4 (a) and (b) which identified the formation of the composites materials. The EDX equally verifies the purity of the synthesized materials which are usually expressed in atomic and weight percentages as presented in table 2.

### Table 2: Elemental composition analysis of Fe₂O₃/SiO₂ nanocomposites

| Samples                   | Element | Weight (%) | Atomic (%) |
|---------------------------|---------|------------|------------|
| Fe₂O₃/SiO₂ @ 200 °C       | O       | 44.35      | 70.40      |
|                           | Si      | 9.53       | 8.62       |
|                           | Fe      | 46.12      | 20.98      |
| Fe₂O₃/SiO₂ @ 250 °C       | O       | 44.98      | 70.19      |
|                           | Si      | 11.80      | 10.49      |
|                           | Fe      | 43.22      | 19.32      |
| Fe₂O₃/SiO₂ @ 300 °C       | O       | 39.91      | 67.31      |
|                           | Si      | 7.66       | 7.36       |
|                           | Fe      | 52.43      | 25.33      |

### Figure 4: Elemental composite distribution of Fe₂O₃/SiO₂ (a) 200 °C (b) 300 °C

### 3.3 X-ray Diffraction (XRD) Analysis of Fe₂O₃/SiO₂

The diffraction pattern of samples was obtained using an X-ray diffractometer, with the diffraction angle set between 10 to 80°. The XRD pattern of the synthesized nanocomposites annealed at different temperatures is illustrated in Figure 6. It can be noted that the synthesized nanocomposites materials have shown a good crystal structure of the Fe₂O₃ as shown in figure 5b which shows the typical phase structure of Fe₂O₃ as prescribed in (JCPDS 88-0866) [11]. This shows the strong binding of the intermolecular forces of iron oxide NPs during chemical reaction with silicon oxide.
Hence, the silica particles during the interaction have not influenced the scattering arrangement of the molecules in iron oxide NPs and that is why the crystallinity of the structure of the iron oxide is maintained in the composite materials as shown in figure 6. Significantly, even when the silica concentrations were high over iron oxide as in the case when the sample annealed at 200 °C (figure 6(a)), the crystallites structure of the iron oxide was still maintained in the composite materials. It can be noted from figure 6 that the strong peaks were displayed at angle 2θ of 30°, 35°, and 63° indicated the promising effect concerning crystallinity developments in those directions, based on that, such angles were selected for the crystal size calculations. Furthermore, it can be seen from Table 3 that the crystal structure of the materials has increased with an increase in temperature. The crystal structure was calculated from peak broadening using Scherrer’s equations as shown below:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

where \( D \) is the crystal size (\( nm \)), \( k \) is the constant dimension shape factor (0.89), \( \lambda \) represent the wavelength of the incident x-ray (0.154 \( nm \)), \( \beta \) the full width of half maximum (FWHM) (radiant) and \( \theta \) diffracted Bragg angle \( \left( \theta = \frac{2\theta}{2} \right) \).

The interplanar \( d \)-spacing (angstrom) was also calculated using Bragg’s law:

\[
n\lambda = 2d \sin \theta
\]

| Table 3: Crystallographic data for Fe$_2$O$_3$/SiO$_2$ composite at different temperatures |
|-----------------|-----------------|-----------------|-----------------|
| Samples         | 2θ(°)           | Crystal plane (h k l) | FWHM (°) | Crystal size, D (nm) | d-spacing (Å) |
|                 |                 |                   |         |                     |               |
| Fe$_2$O$_3$/SiO$_2$ _200 °C |                 |                   |         |                     |               |
| 30              | (2 2 0)         | 0.36              | 23     | 0.29                |               |
| 35              | (3 1 1)         | 0.33              | 25     | 0.25                |               |
| 63              | (4 4 0)         | 0.47              | 20     | 0.14                |               |
| Fe$_2$O$_3$/SiO$_2$ _250 °C |                 |                   |         |                     |               |
| 30              | (2 2 0)         | 0.35              | 24     | 0.29                |               |
| 35              | (3 1 1)         | 0.31              | 27     | 0.25                |               |
| 63              | (4 4 0)         | 0.40              | 23     | 0.14                |               |
| Fe$_2$O$_3$/SiO$_2$ _300 °C |                 |                   |         |                     |               |
| 30              | (2 2 0)         | 0.38              | 26     | 0.29                |               |
| 35              | (3 1 1)         | 0.32              | 30     | 0.35                |               |
| 63              | (4 4 0)         | 0.51              | 27     | 0.32                |               |
3.4 Fourier-Transform Infrared Spectroscopy (FTIR) of Fe$_2$O$_3$/SiO$_2$

FT-IR spectrum of Fe$_2$O$_3$/SiO$_2$ nanocomposites calcined at 200 °C and 300 °C is shown in Figure 7 (a) and (b) respectively, the peaks at 3428 for both samples indicated the presence of O–H groups on the surface of the particles. The water absorption on the surface of the materials can be observed at the peak of 1627 and 1637 cm$^{-1}$ for samples at 200 °C and 300 °C respectively [12]. Fe–O bond manifested at the absorption peak of 556 and 548 cm$^{-1}$ for the composite material at 200 °C and 300 °C respectively. The vibrational stretching of Si–O bonds can be identified at the peak of 1082 cm$^{-1}$ and that of Si-OH at 633 cm$^{-1}$ for the sample annealed at 200 °C and when the sample annealed at 300 °C Si–O bonds can be observed at 1082 cm$^{-1}$ and that of Si-OH at 640 cm$^{-1}$ [10].

**Figure 5**: XRD pattern (a) SiO$_2$ (b) Fe$_2$O$_3$

**Figure 6**: XRD analysis of Fe$_2$O$_3$/SiO$_2$ at different temp. (a) 200 °C (b) 250 °C (c) 300 °C


4. Conclusion

The composite materials of Fe$_2$O$_3$/SiO$_2$ were synthesized via the sol-gel method and annealed at different temperatures (200, 250, and 300 °C) to evaluate the temperature effects on the crystal and morphological sizes of the composite material. The crystal size of the composite material was calculated and found to be increasing significantly with an increase in annealing temperature. It has been observed from FESEM analysis, the particle size was equally found to increase with an increase in temperatures. The elemental composite distribution and purity of the materials were confirmed by EDX. The chemical reaction of the composite materials was analyzed by FTIR, in which the functional groups of OH and expected chemical bonds of Fe–O, and Si–O have been observed. Hence, the annealing temperature is the reliable method of increasing the crystal and morphological sizes of Fe$_2$O$_3$/SiO$_2$ nanocomposites materials.
5. References

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