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Research Article

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The Effect of Temperature on Iron Oxide Nanoparticle Sizes, Shape and Composition Synthesized through Direct Oxidative Alkaline hydrolysis

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Abstract Iron oxide nanoparticles play important rolein medical, environmental, and other scientific applications. The size of the nanoparticles determines its suitability for different applications, and this is determined by the synthesis technique adopted and operating conditions. The aim of this work is to synthesis iron oxide (Fe_3O_4 Nps) nanoparticles also known as magnetite nanoparticles through oxidative alkaline hydrolysis of iron II sulphate salt, and explore the effect of synthesis temperature on the sizes and composition of the nanoparticles. The result from the experiments carried out showed that change in operating temperature does not really affects the size and shape of the nanoparticles and the nanoparticles had cubic shape at temperatures 50, 90 and 150 °C, with sizes 55, 53 and 52 nm respectively. Temperature above 150 °C did not favour the stabilization of the nanoparticles as the solution turns oily due to degradation of PEI. The result from the X-ray diffractometer showed that at 150 °C, (α–Fe_2O_3) called hematite was formed as by product of the reaction. X-ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy were used in characterizing the nanoparticles.

Keywords Iron oxide nanoparticles, Temperature, Sizes, X-ray diffraction, X-ray photoelectron spectroscopy

Introduction

Iron oxide nanoparticles especially magnetite (Fe_3O_4Nps) nanoparticles are very important because of its applications in medical, environmental and scientific fields. Its use depends greatly on the nanoparticles sizes and other factors such as composition, stability, purity which are influenced by the nanoparticles mode of synthesis. Different techniques are employed to synthesize magnetite nanoparticles such as sol gel, sonochemical reactions, hydrothermal reactions, co-precipitation, microemulsions, flow injection and electro spray method [1-5]. Each technique has unique characteristics that affect the nanoparticles properties and the choice of technique depends on the type of application the nanoparticles are used for.

This research work looks at the effect of operating temperatures on the sizes, shape and composition of magnetite nanoparticles synthesized through direct oxidative alkaline hydrolysis of iron II sulphate salt. In oxidative alkaline hydrolysis of Iron II salt, the salt is reacted with a strong base (sodium hydroxide) with mild reducing agent (potassium hydroxide) to form iron (II) hydroxide. The iron (II) hydroxide is further heated and undergoes anaerobic oxidation by the protons of water to form magnetite and molecular hydrogen. Stabilizers are often used to stabilize the magnetite nanoparticles to improve the mono-dispersity and stability of the particles. This research work used polyethyleneimine (PEI) a polycation as the nanoparticles stabilizing agent.

Research work has been carried out on the synthesis of iron oxide nanoparticles (Fe_3O_4) through other methods and through oxidative alkaline hydrolysis of iron II sulphate salt [6-8]. Their interest has been on the synthesis of desired Fe_3O_4 nanoparticles sizes, types of stabilizers and their role on the nanoparticles and application of the

nanoparticles in field of interest. Less attention has been focussed on the effect varying temperature on the nanoparticles sizes, nature and composition when synthesized through oxidative alkaline hydrolysis..

Materials and Methods

Iron II sulphate heptahydrate >99 %, and Polyethyleneimine (branched 25000 mw) was purchased from Sigma Aldrich (Dorset UK), sodium hydroxide 97 %, and potassium nitrate 99 % were bought from Alfa Aesar (Lancashire UK). Millipore deionised water was used for preparation of all solutions.

The nanoparticles were synthesized by adopting similar procedures from Goon *et al* [9] for the synthesis of iron oxide nanoparticles through oxidative alkaline hydrolysis. Briefly, 0.025M of iron (II) sulphate heptahydrate was placed inside a 250 ml beaker containing 80ml of deionized water mixed with 500mg/l PEI and sparged for 20 minutes. Followed by the addition of Potassium nitrate (10 ml, 2 M) and sodium hydroxide (10 ml, 1 M). This results in the formation of iron (II) hydroxide which was heated for 2 hours at varying temperatures of 50, 90 and 150 ^{o}C respectively while constantly sparging the system with nitrogen. The black precipitate of iron oxide nanoparticles formed was washed several times with deionised water and the nanoparticles finally suspended in 80 ml of deionised water at pH 7.0.

Characterization of the nanoparticles where done using X-ray diffraction pattern with PANalytical X'pert Pro MPD, using Cu Kα radiation with wavelength of 1.54180Å to determine the crystalline structure of the nanoparticles. X-ray photoelectron spectroscopy (XPS) with Thermo Scientific K-α monochromated small spot X-ray was used to determine the nature and core electrons of the Fe_3O_4 nanoparticles. Transmission electron microscopy analysis (TEM) was done with Philips CM200 FEGTEM field emission gun TEM/STEM with supertwin objective lens to determine the shape and sizes of the nanoparticles.

Results and Discussion

Figure 1 shows the paramagnetic properties of the synthesized iron oxide nanoparticles towards an external magnetic field. In Fig. 1a the nanoparticles were stabilized in solution with PEI and Fig. 1b shows the nanoparticles been attracted to a magnetic field. The nanoparticles dispersed back in the solution when the magnetic field is removed. Figure 1c shows the TEM image of the nanoparticles synthesized with 0.025M iron salt at 90°C, with average size particles of 55 nm. The shape of the nanoparticles is cubic same applies for 50°C and 150°C.

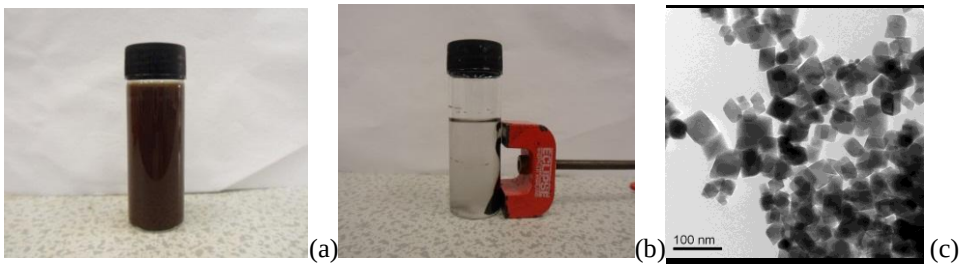

Figure 1: paramagnetic property of the synthesized iron oxide nanoparticles

Figure 2a shows the XPS result for magnetite nanoparticles synthesized at 0.025M $FeSO_4$. The Figure shows the characteristic doublet for iron base compounds indicating the presence of 2p core electrons (Fe $2p_{3/2}$ and $2p_{1/2}$). The arrows in the Figure shows the presence of iron II cation (Fe^{2+}) at binding energies of 710.18eV, 713.38eV and 721.78eV and iron III cation (Fe^{3+}) at 718.08eV confirming the formation of magnetite (Fe_3O_4 Nps) nanoparticles. Figure 2b shows that the 1s core electron of oxygen in Fe_3O_4 nanoparticles results only from oxides in the nanoparticles at lower binding peak of 529.58eV and 530.48eV.

Table 1 shows the effect of changing temperature on Iron oxide nanoparticles synthesized through oxidative alkaline hydrolysis. The result shows that synthesizing the nanoparticles at different temperatures does not really affect the sizes .But the XRD diffraction pattern of the nanoparticles in Figure 3 showed the appearance of diffraction peak **a**-012 at lower angle planes around 24^{o} when the temperature of the system was increased to 150^{o}C. This peak indicates the presence of α –Fe_2O_3 (hematite) which is a more stable iron III oxide. This might result from the oxidation of Fe_3O_4at higher temperature (150°C). The other diffraction peak (111, 220, 311, 222, 400, 422, 511, 440 and 622) indicates formation of Fe_3O_4 Nps.

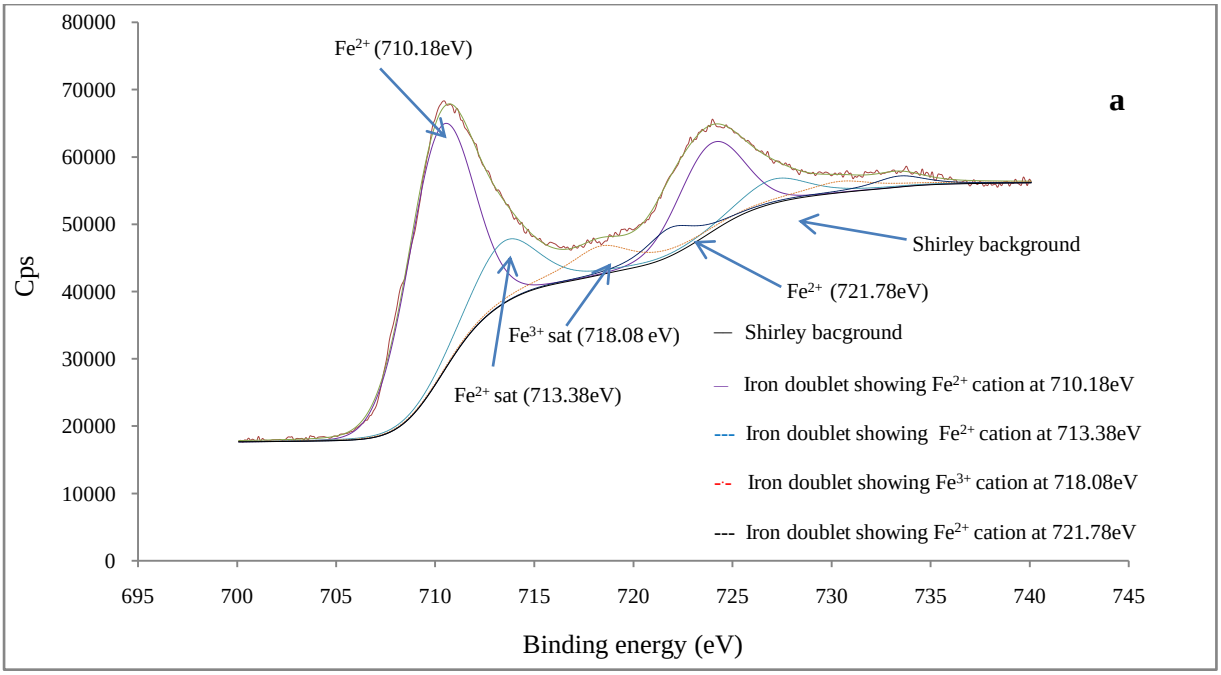

Figure 2: Fe_3O_4 nanoparticles XPS analysis (a) 2p core electrons (b) 1s core electrons of O_2

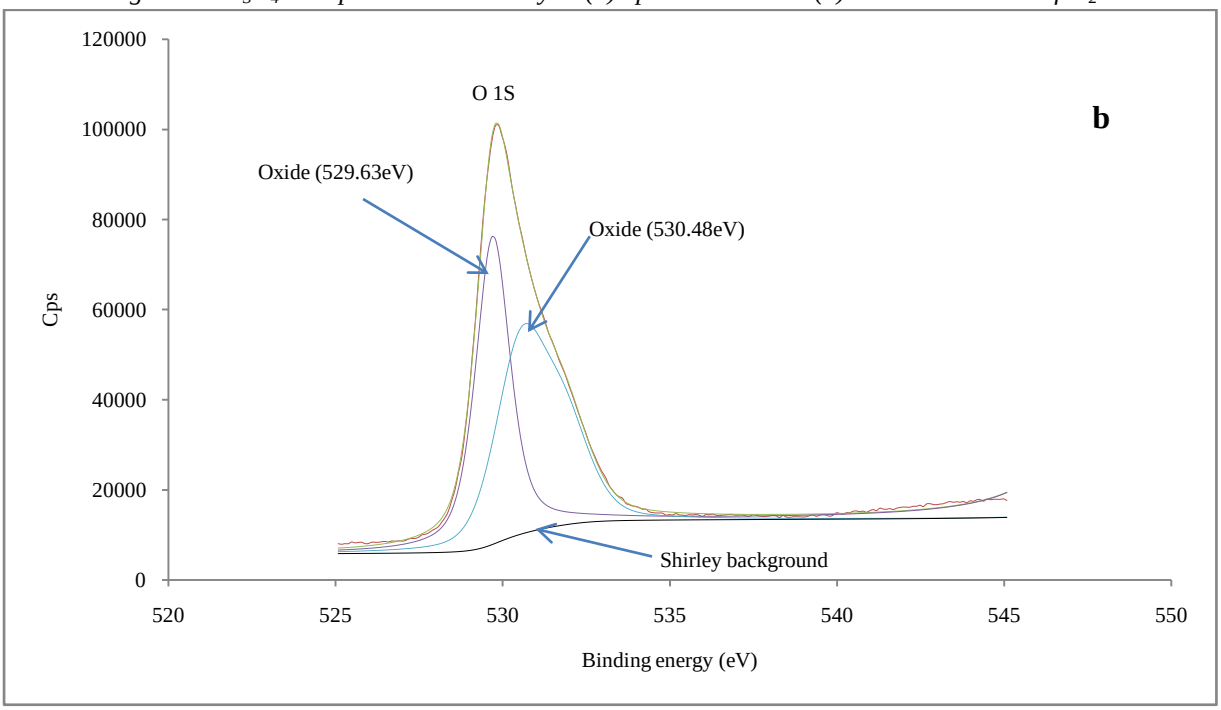

Table 1: Fe_3O_4 nanoparticles synthesized by varying synthesis temperature

Iron II sulphate (M)	Potassium nitrate (M)	Sodium hydroxide (M)	Temp (Deg.)	PEI (g/l)	Average particle size (nm)
0.025	2.0	1.0	50	500	55
0.025	2.0	1.0	90	500	53
0.025	2.0	1.0	150	500	52

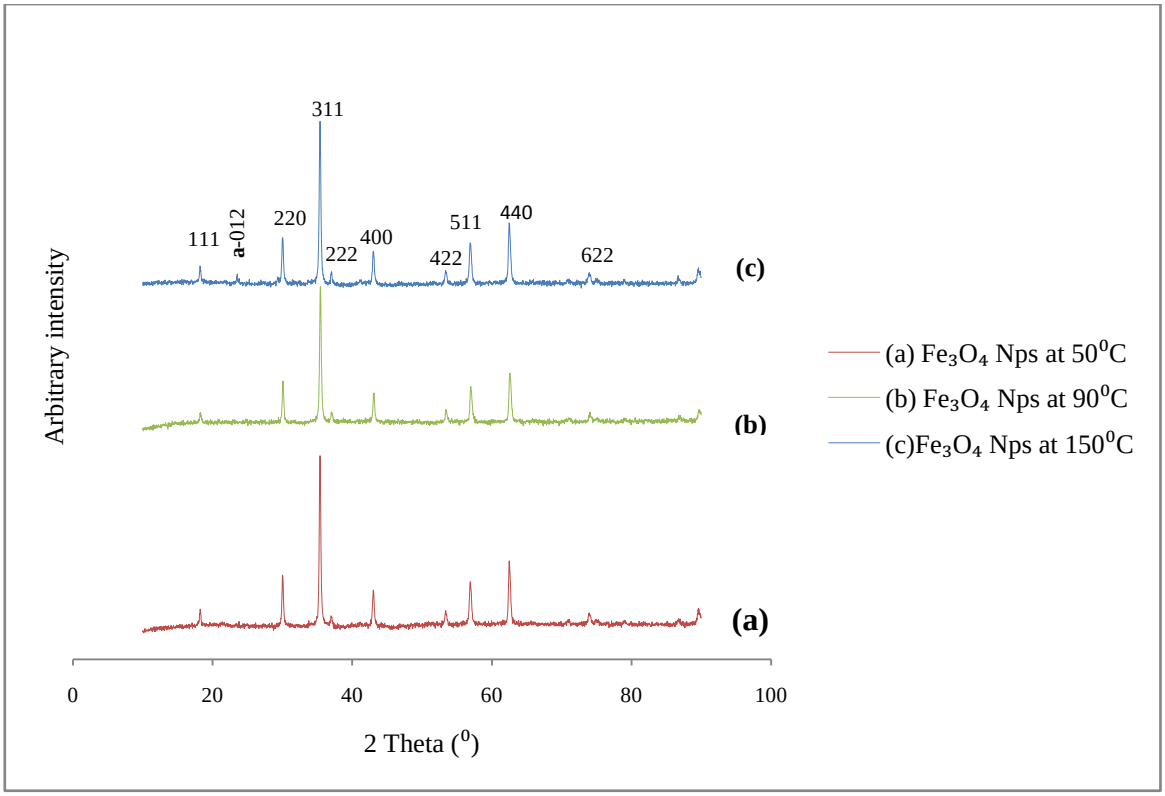

Figure 3: XRD analysis Fe_3O_4 synthesized by varying synthesis temperatures (a) 50°C, (b) 90°C and (c) 150°C

Conclusion

The result showed that iron oxide nanoparticles was successfully synthesized through oxidative alkaline hydrolysis of iron salt and characterized. The change in operating temperature does not really affects the size and shape of the nanoparticles and it was observed experimentally the nanoparticles had cubic shape at temperatures 50, 90 and 150 °C. The nanoparticles sizes at these temperatures are 55, 53 and 52 nm respectively. The result from the X-ray diffractometer showed that at 150 °C, a more stable form of iron III oxide (α –Fe_2O_3) called hematite was formed as by product of the reaction. Also temperatures above 150 °C does not favour the stabilization of the nanoparticles as the solution turns oily due to degradation of the PEI.

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