DIRECT SYNTHESIS OF WATER-SOLUBLE NICKEL FERRITE NANOPARTICLES ($NiFe_2O_4$) BY THE THERMOLYSIS OF A SINGLE SOURCE PRECURSOR.

Supported by tetfund TERTIARY EDUCATION TRUST FUND

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Received: September 21, 2022 **Accepted:** November 12, 2022

Abstract:

In this paper, highly crystalline and water dispersible nickel ferrite nanoparticles were synthesised by the hot injection thermolysis of heterometallic pivalate cluster ($[Fe_2NiO(O_2C^tBu)_6(HO_2C^tBu)_3]$) in triethylene glycol (solvent) and polyvinyl pyrrolidone (capping agent) at the boiling point of the solvent (285 °C.) The nanoparticles were characterised by Powder X-ray Diffraction (p-XRD), Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) and Energy Dispersive Spectroscopy (EDS). The p-XRD showed crystalline pure phase of nickel ferrite nanoparticles and TEM revealed a spherical morphology of average size 7.0 ± 0.7 nm. The as synthesised nanoparticles are directly water dispersible without any post modification process.

Keywords: nickel ferrite nanoparticles, colloidal, water dispersible, single source precursor, monodisperse, thermal decomposition.

Introduction

The numerous applications of ferrites in the biomedical area,(Ravichandran and Velumani, 2020) data storage,(Hu *et al.*, 2012) sensors,(Šutka and Gross, 2016) catalyst in energy conversion (Navadeepthy *et al.*, 2021) and environmental clean-up,(Mahmoodi, 2016) (Sun, Han and Chen, 2019) have made them received a lot of interest in the last decade. This is especially true for water soluble nickel ferrite ($NiFe_2O_4$) nanoparticles, which may have their sizes altered and their surfaces functionalized with the right molecules to make them highly selective for their intended targets, making them ideal for biomedical and environmental applications. Additionally, their superparamagnetic characteristics allow for the control of their motion when subjected to an external magnetic field. Nickel ferrite nanoparticles are one of the important materials with inverse spinel structures having typical ferromagnetic properties, high electrical resistivity, moderate saturation magnetisation and they are readily available.(Li *et al.*, 2012)·(Mathew and Juang, 2007). As a result, many methods have been used for their fabrication including co-precipitation,(Dalai *et al.*, 2019) hydrothermal,(Nejati and Zabihi, 2012)(Liu *et al.*, 2016,) micro-emulsion,(Rodríguez-Rodríguez *et al.*, 2019) sol-gel,(Kesavamoorthi *et al.*, 2016) microwave assisted,(Simon *et al.*, 2021) green synthesis (Kulkarni *et al.*, 2020) sonochemical (Amulya *et al.*, 2020) and thermal decomposition.(Stoia *et al.*, 2012 Mohapatra, Rout and Panda, 2011; Naidek *et al.*, 2011) More often, these nanoparticles are well suited for biological and environmental applications in monodisperse form, hence the research on getting narrow size distribution that are well dispersed in aqueous medium is still ongoing.

Although it has been demonstrated that thermal decomposition techniques can yield monodisperse crystalline nanoparticles (Hyeon *et al.*, 2001)·(Sun and Zeng, 2002)· one drawback of this approach is that the nanoparticles are frequently insoluble in water due to the hydrophobic properties of the capping agents which in turn has restricted the nanoparticles' use in the biological and environmental domains. Water dispersible ferrite nanoparticles with appropriate characteristics must be created in order to solve this issue and this can be attained through direct synthesis or post-synthesis via ligand exchange.

In order to disperse the as-synthesised nanoparticles in an aqueous medium, numerous post-synthesis surface modification and ligand exchange techniques have been used. (Wang *et al.*, 2003; Huh *et al.*, 2005; Jun *et al.*, 2005; Li, Afzaal and O'Brien, 2006; Yu *et al.*, 2008) However, one of the major drawbacks of this method is the incomplete ligand replacements that result in eventual precipitation out of the aqueous solution. As a result, it is preferred to directly synthesize highly-crystalline ferrite nanoparticles that are soluble in water.

Only very limited research has been reported on the direct synthesis of water-soluble nickel ferrite nanoparticles from a single source precursor. In this paper, we demonstrate the thermolysis of a heterometallic pivalate cluster ($[Fe_2NiO(O_2C^tBu)_6(HO_2C^tBu)_3]$) in triethylene glycol as solvent and polyvinyl pyrrolidone (capping agent) to produce crystalline and water-dispersible nickel ferrite nanoparticles at 285 °C (the boiling point of the solvent).

Materials and Methods.

Synthesis of Precursor.

The synthesis of $[Fe_2NiO(O_2C^tBu)_6(HO_2C^tBu)_3]$ was carried out as described in the literature.(Abdulwahab *et al.*, 2014)

Synthesis of Nanoparticles.

The hot injection thermolysis method was used in the synthesis of the nanoparticles. In a typical synthesis, triethylene glycol TREG (15 mL) and polyvinylpyrrolidone PVP (M_w 40,000 0.25 g) were degassed at 100 ºC under

vacuum for 30 minutes before heating the mixture to the boiling point of the solvent (TREG) under nitrogen. Then, 0.275 g (0.25 mmol) of the precursor $[Fe_2NiO(O_2C^tBu)_6(HO_2C^tBu)_3]$ was dissolved in TREG (10 mL) and injected into the solution of the hot mixture. The reaction was maintained at 230 ºC for 3 hours. The resulting mixture was allowed to cool and acetone was added to precipitate the nanoparticles which were then isolated by centrifugation. The residue was washed with acetone three times and then re-dispersed in deionised water.

Characterisation of Nanoparticles.

Powder X-ray diffraction studies were performed on a Bruker Discover 8 diffractometer with a Co- Kα radiation. TEM samples were prepared by placing 1 or 2 drops of the nanoparticle's dispersion on a holey carbon copper grid. High resolution transmission electron microscopy (HRTEM) was performed using a Tecnai F30 FEG TEM instrument at an accelerating voltage of 300 kV.

Results and Discussion.

The p-XRD patterns of the nanoparticles obtained were matched with cubic trevorite- nickel iron oxide ($NiFe_2O_4$) (ICDD Card No: 00-054-0964) (**Fig. 1 (a)**). The Debye Scherrer equation was used to calculate the average crystallite size and found to be 6.5 nm. The TEM images (**Fig. 1 (b)**). showed nanoparticles of size distribution 7.0 ± 0.7 nm which is in good agreement with the size calculated from Debye Scherrer formula.

The crystallinity of the sample is also apparent in their lattice fringes with *d*-spacing value of 4.81 Å (**Fig. 1(c)**) which corresponds to the (111) reflection plane. It is worth mentioning that the average *d*- spacing of the nanoparticles was calculated from a number of lattice fringes by drawing a perpendicular line across the fringes which produced a line profile from which the spacing is estimated (**Fig. 1(e)**). The diffraction patterns also confirmed the purity and crystallinity of the trevorite nanoparticles with strong diffraction rings matching the (220), (311) and (400) planes of the cubic phase (**Fig. 1(d)**). The EDX analysis showed the presence of both nickel and iron in the ratio of 1: 0.5 corroborating the p-XRD data (**Fig. 2**).

The formation of monodispersed nickel ferrite nanoparticles has been attributed to the stabilisation provided by the PVP which is achieved by controlling the growth and preventing aggregation of nanoparticles resulting from Van der Waals forces during and after the synthesis via steric stabilization. (Naseri *et al.*, 2011)·(Goodarz Naseri, Saion and Khalil Zadeh, 2013). In addition, the hot injection method is able to produce monodisperse nanoparticles because there is a clear separation between nucleation and growth process which is necessary for the production of a narrow size distribution. The principle is that the cold solution of precursor which is rapidly injected into a hot, high boiling point solvent and capping agent mixture induces a supersaturated solution that leads to a burst of nucleation leading to the depletion of monomers in solution thus halting subsequent nucleation and then the growth process follows.

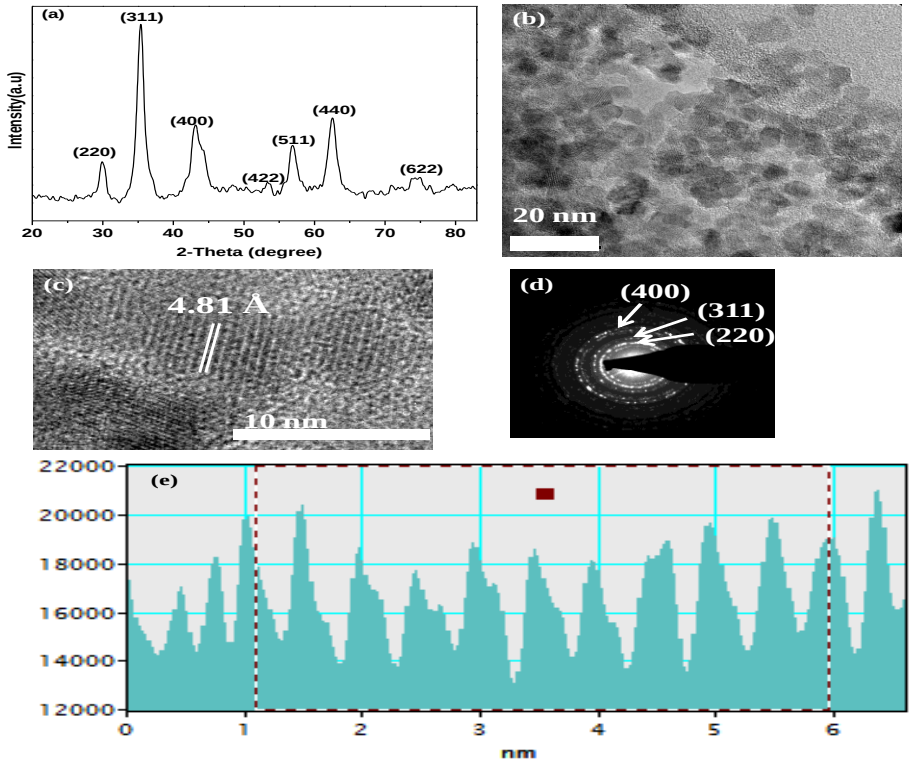

Fig. 1 (a) p-XRD pattern for cubic nickel iron oxide nanoparticles ($NiFe_2O_4$). (b) TEM images (c) HRTEM showing lattice fringes. (d) Diffraction rings obtained from (b). (e) Line profile used for calculating the *d*-spacing from (c).

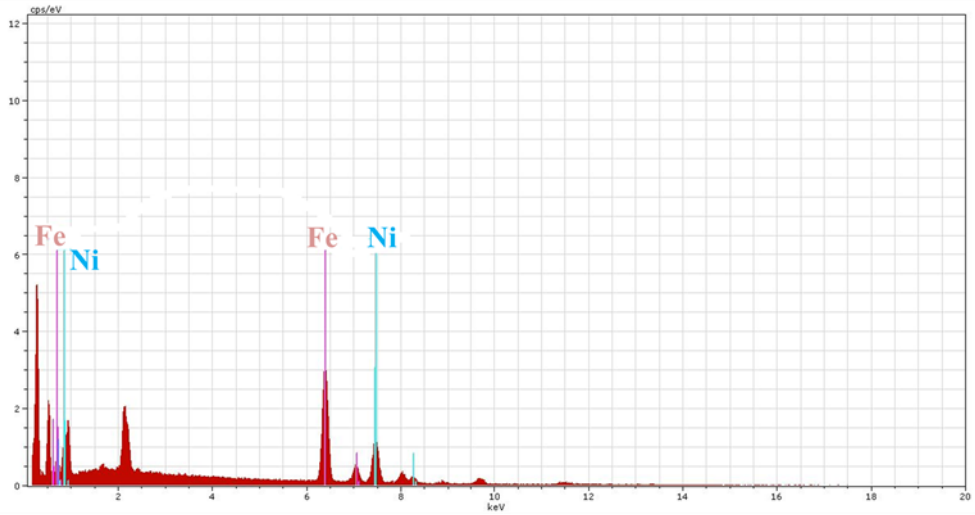

Fig. 2 EDX spectrum of nickel ferrite nanoparticles.

Conclusion.

The hot injection thermolysis process was successfully used to produce water-dispersible nickel ferrite nanoparticles from heterometallic pivalate clusters. Without using any size-selective precipitation after synthesis, an excellent size distribution was directly achieved. The p-XRD, SAED, and HRTEM pictures of the nickel ferrite nanoparticles revealed that they were formed as pure single-phase materials. At room temperature, the nanoparticle dispersion remained stable for many months. Our research showed that these nanoparticles could have potential use in biomedical and environmental applications.

Acknowledgement.

K.O. Abdulwahab would like to appreciate the financial support from the Islamic Development Bank, Saudi Arabia.

References.

Abdulwahab, K. O. *et al.* (2014) 'Hot injection thermolysis of heterometallic pivalate clusters for the synthesis of monodisperse zinc and nickel ferrite nanoparticles', *Journal of Materials Chemistry C*, 2(33), p. 6781. doi: 10.1039/C4TC00832D.

Amulya, M. A. S. *et al.* (2020) 'Sonochemical synthesis of NiFe2O4 nanoparticles: Characterization and their photocatalytic and electrochemical applications', *Applied Surface Science Advances*, 1(August). doi: 10.1016/j.apsadv.2020.100023.

Dalai, N. *et al.* (2019) 'Highly Active Ternary Nickel–Iron oxide as Bifunctional Catalyst for Electrochemical Water Splitting', *ChemistrySelect*, 4(27), pp. 7791–7796. doi: 10.1002/slct.201901465.

Goodarz Naseri, M., Saion, E. and Khalil Zadeh, N. (2013) 'The amazing effects and role of PVP on the crystallinity, phase composition and morphology of nickel ferrite nanoparticles prepared by thermal treatment method', *International Nano Letters*, 3(1), p. 19. doi: 10.1186/2228-5326-3-19.

Hu, W. *et al.* (2012) 'Opportunity of spinel ferrite materials in nonvolatile memory device applications based on their resistive switching performances', *Journal of the American Chemical Society*, 134(36), pp. 14658–14661. doi: 10.1021/ja305681n.

Huh, Y. M. *et al.* (2005) 'In vivo magnetic resonance detection of cancer by using multifunctional magnetic nanocrystals.', *Journal of the American Chemical Society*, 127(35), pp. 12387–91. doi: 10.1021/ja052337c.

Hyeon, T. *et al.* (2001) 'Synthesis of highly crystalline and monodisperse maghemite nanocrystallites without a size-selection process.', *Journal of the American Chemical Society*, 123(51), p. 12798. Available at: http://www.ncbi.nlm.nih.gov/pubmed/22754999.

Jun, Y. W. *et al.* (2005) 'Nanoscale size effect of magnetic nanocrystals and their utilization for cancer diagnosis via magnetic resonance imaging.', *Journal of the American Chemical Society*, 127(16), pp. 5732–3. doi: 10.1021/ja0422155.

Kesavamoorthi, R. *et al.* (2016) 'Synthesis and characterization of nickel ferrite nanoparticles by sol - Gel auto combustion method', *Journal of Chemical and Pharmaceutical Sciences*, 9(1), pp. 160–162.

Kulkarni, G. D. *et al.* (2020) 'Green synthesis of NiFe2O4 nanoparticles using different fuels and their structural characterization', *Journal of Physics: Conference Series*, 1644(1). doi: 10.1088/1742-6596/1644/1/012003.

Li, X. *et al.* (2012) 'Nanostructural and magnetic studies of virtually monodispersed NiFe2O4 nanocrystals synthesized by a liquid–solid-solution assisted hydrothermal route', *Journal of Nanoparticle*

Research, 14(3), pp. 751–759. doi: 10.1007/s11051-012-0751-6.

Li, Y., Afzaal, M. and O'Brien, P. (2006) 'The synthesis of amine-capped magnetic (Fe, Mn, Co, Ni) oxide nanocrystals and their surface modification for aqueous dispersibility', *Journal of Materials Chemistry*, 16(22), p. 2175. doi: 10.1039/b517351e.

Liu, G. *et al.* (2016) 'Fabrication of mesoporous NiFe2O4 nanorods as efficient oxygen evolution catalyst for water splitting', *Electrochimica Acta*, 211, pp. 871–878. doi: 10.1016/j.electacta.2016.06.113.

Mahmoodi, N. M. (2016) 'Photocatalytic degradation of textile dyes using ozonation and magnetic nickel ferrite nanoparticle', *Progress in Color, Colorants and Coatings*, 9(3), pp. 163–171.

Mathew, D. S. and Juang, R.-S. (2007) 'An overview of the structure and magnetism of spinel ferrite nanoparticles and their synthesis in microemulsions', *Chemical Engineering Journal*, 129(1–3), pp. 51–65. doi: 10.1016/j.cej.2006.11.001.

Mohapatra, S., Rout, S. R. and Panda, A. B. (2011) 'One-pot synthesis of uniform and spherically assembled functionalized MFe2O4 (M=Co, Mn, Ni) nanoparticles', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384(1–3), pp. 453–460. doi: 10.1016/j.colsurfa.2011.05.001.

Naidek, K. P. *et al.* (2011) 'Structure and morphology of spinel MFe2O4 (M=Fe, Co, Ni) nanoparticles chemically synthesized from heterometallic complexes.', *Journal of Colloid and Interface Science*, 358(1), pp. 39–46. doi: 10.1016/j.jcis.2011.03.001.

Naseri, M. G. *et al.* (2011) 'Simple preparation and characterization of nickel ferrite nanocrystals by a thermal treatment method', *Powder Technology*, 212(1), pp. 80–88. doi: 10.1016/j.powtec.2011.04.033.

Navadeepthy, D. *et al.* (2021) 'Boosting the kinetics of oxygen and hydrogen evolution in alkaline water splitting using nickel ferrite /N-graphene nanocomposite as a bifunctional electrocatalyst', *International Journal of Hydrogen Energy*, 46(41), pp. 21512–21524. doi: 10.1016/j.ijhydene.2021.03.244.

Nejati, K. and Zabihi, R. (2012) 'Preparation and magnetic properties of nano size nickel ferrite particles using hydrothermal method.', *Chemistry Central Journal*, 6(1), pp. 23–28. doi: 10.1186/1752-153X-6-23.

Ravichandran, M. and Velumani, S. (2020) 'Manganese ferrite nanocubes as an MRI contrast agent', *Materials Research Express*, 7(1). doi: 10.1088/2053-1591/ab66a4.

Rodríguez-Rodríguez, A. A. *et al.* (2019) 'Spinel-type ferrite nanoparticles: Synthesis by the oil-in-water microemulsion reaction method and photocatalytic water-splitting evaluation', *International Journal of Hydrogen Energy*, pp. 12421–12429. doi: 10.1016/j.ijhydene.2018.09.183.

Simon, C. *et al.* (2021) 'Magnetic NiFe2O4 Nanoparticles Prepared via Non-Aqueous Microwave-Assisted Synthesis for Application in Electrocatalytic Water Oxidation', *Chemistry - A European Journal*, 27(68), pp. 16990–17001. doi: 10.1002/chem.202101716.

Stoia, M. *et al.* (2012) 'Synthesis of nanocrystalline nickel ferrite by thermal decomposition of organic precursors', *Journal of Thermal Analysis and Calorimetry*, 108(3), pp. 1033–1039. doi: 10.1007/s10973-011-1903-0.

Sun, M., Han, X. and Chen, S. (2019) 'Synthesis and photocatalytic activity of nano-cobalt ferrite catalyst for the photo-degradation various dyes under simulated sunlight irradiation', *Materials Science in Semiconductor Processing*, 91(December 2018), pp. 367–376. doi: 10.1016/j.mssp.2018.12.005.

Sun, S. and Zeng, H. (2002) 'Size-Controlled Synthesis of Magnetite Nanoparticles', *Journal of the American Chemical Society*, 124(31), pp. 8204–8205.

Šutka, A. and Gross, K. A. (2016) 'Spinel ferrite oxide semiconductor gas sensors', *Sensors and Actuators, B: Chemical*, 222, pp. 95–105. doi: 10.1016/j.snb.2015.08.027.

Wang, Y. *et al.* (2003) '"Pulling" Nanoparticles into Water: Phase Transfer of Oleic Acid Stabilized Monodisperse Nanoparticles into Aqueous Solutions of α-Cyclodextrin', *Nano Letters*, 3(11), pp. 1555–1559. doi: 10.1021/nl034731j.

Yu, C. *et al.* (2008) 'A novel method to prepare water-dispersible magnetic nanoparticles and their biomedical applications: magnetic capture probe and specific cellular uptake.', *Journal of Biomedical Materials Research*, 87(2), pp. 364–72. doi: 10.1002/jbm.a.31786.