

A Green and Economic Manufacturing Process of Magnetite Nanoparticle, Iodine Crystals and Table Salt by One Reaction

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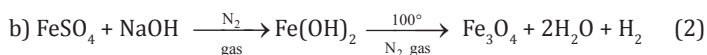
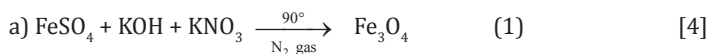
Abstract

An innovative quantitative synthetic method for preparing magnetite nanoparticles, iodine crystals and table salt was achieved by co-precipitation in aqueous solution using only one single iron (III) salt as a precursor. A 2 Fe (III):1 Fe (II) mole ratio was first attained in solution by reducing iron(III) using KI solution, followed by filtering the iodine formed and subliming it then hydrolyzing the filtrate by sodium hydroxide solution at pH 9 to 11. A high selectivity and atom economy percents were achieved indicating that the method is environmentally benign and green. A high quantitative yield of magnetite, iodine and table salt was obtained. The as-synthesized magnetite nanoparticles were characterized by fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), field emission transmission electron microscopy (FETEM), selected area electron diffraction (SAED), and ⁵⁷Fe Mossbauer spectroscopy. Magnetite nanocrystals (d: 7.84 ± 0.05 nm) and nanorods (d: 6.3 ± 0.2 nm; l: 46.2 ± 0.9) formation was evident. Iodine crystals of 100% purity were obtained by sublimation. Table salt was then crystallized from the final filtrate.

Keywords: Magnetite; Nanocubes; Nanorods; Co-precipitation; Hydrolysis; Selectivity; Atom economy

Introduction

Synthesis, characterization and applications of iron oxide nanocrystals have received tremendous attention in recent years due to their potentials for information storage devices, rotary shaft sealing, position sensing [1] as well as medical and pharmaceutical applications [2]. Several methods are known in the art for the synthesis of magnetite, Fe₃O₄. Cornwell and Schwertmann [3] have reported several synthetic methods all of which require more than one iron component as precursors, several chemical reagents, inert atmosphere, special apparatus and/or restricting conditions. Exemplary methods are shown as follows.



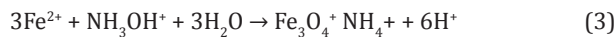
(produces complicating side effect) [5]

c) Reduction of hematite at 400°C in an atmosphere of 5% H₂/95% Ar, saturated with water vapour free of O₂ [6].

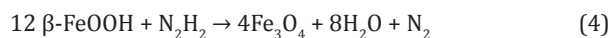
d) Reaction of a 1:2 Fe(II)/ Fe(III) solution, under alkaline conditions at 80°C under N₂ [6].

e) Reaction at 85°C of Fe(II) ammonium sulphate solution (buffered to pH 7 to 8 with sodium acetate) with hydroxylamine sulphate; the suspension is held under N₂ gas [7] as shown thus:

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f) Reductive transformation in a sealed ampoule of an akaganeite suspension in the presence of hydrazine at pH 9.5 to 11.5 and 100°C [8]. (Blesa and Maroto, 1986).



g) Decomposition of an alkaline (0.2 to 0.4 MOH) solution of Fe (III) NTA at 217°C in an autoclave [9].

h) Heating of iron hydroxide acetate at 200 to 260°C under N₂ [10].

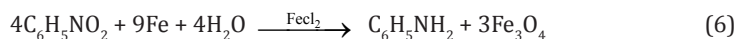
i) Boiling a mixture of Fe(II) sulphate and bispyridoxylidene hydrazine phthalazine for 10 min at pH 7 [11].

j) Thermal decomposition of Fe(II) sulphide in air at 500°C, which is environmentally unfriendly [12].



k) Holding a solution of Fe (III) acetylacetonate in 1-propanol under N₂ in an autoclave at 300°C for several hours [13].

l) Reduction of nitrobenzene to aniline produces Fe₃O₄ [14] as shown thus:



Further, several Fe₃O₄ synthetic methods were patented [15-21].

The most popular methods for the synthesis of the spinel structured Fe₃O₄ include co-precipitation in aqueous solution by adding hydroxides into iron salt solutions [22,23] and the thermal decomposition of iron organometallic compounds in high boiling organic solutions in the presence of stabilizers [24,25].

Recently, Xu, *et al.* [25] reported on the organic phase synthesis of mono dispersed iron oxide nano crystals using iron chloride as a precursor.

In this paper, a report was made on an innovative invention [26] that relates to a process of preparing magnetite nanocrystals by the co-precipitation method using iron (III) chloride or nitrate salts as precursors. The objective of this invention is to provide a process of preparing magnetite (Fe₃O₄) and derivatives thereof, not reported herein, which overcomes the drawbacks of the prior art, especially a process which only requires one iron compound as the starting precursor, a limited number of additional chemical reagents, and a process which can be carried out under simple reaction conditions, preferably at room temperature, with easy work-up of the product obtained.

Experimental

Starting Material

Iron chlorides (FeCl₃ and FeCl₃.6 H₂O) were purchased from WINLAB, Leicestershire, England. Iron nitrate (Fe (NO₃)₃.9H₂O) sodium hydroxide (NaOH) and 25% ammonia solution were all purchased from BDH, Poole, England. And potassium iodide (KI) and polyvinyl alcohol (PVA 72000) were purchased from MERCK, Darmstadt, and F. R. Germany.

Characterization

The FTIR spectrum was recorded on a Shimadzu FTIR-8400S, Prestige-21 spectrophotometer in a KBr matrix. Powder X-ray diffraction (XRD) pattern was obtained with an Ultima IV X-ray diffractometer using copper-monochromatized Cu Kα 1 radiation under the acceleration voltage of 40 kV and a current of 40 mA. The morphology of the Fe₃O₄ nanocrystals was examined by a JEOL JSM-6380 LA scanning electron microscope and a JEOL, TEM-2100F transmission electron microscope with an acceleration voltage of 200 kV. ⁵⁷Fe Mossbauer spectra were recorded in the Institute des Molecules et Mate'riaux du Mans (IMMM), University' du Maine, France.

Synthesis of magnetite nanoparticles

The work-up consists of mixing iron(III) salt solution with potassium iodide aqueous solution in a 3:1 mole ratio, filtering out the iodine formed, hydrolyzing the filtrate with either sodium hydroxide or ammonia solution, filtering the black magnetite precipitate, washing with water and drying at 250°C.

An exemplary experiment is carried out as follows

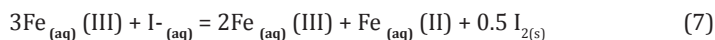
19.46g (0.119 mol) of anhydrous FeCl_3 was completely dissolved in 150 ml distilled water to prepare aqueous solution A. Further, 6.584g (0.0396 mol) of potassium iodide was dissolved in 50.0 ml of distilled water to prepare aqueous solution B. Solutions A and B were then mixed together at room temperature, stirred and allowed to reach equilibrium for one hour. The precipitate of iodine was filtered out, washed with distilled water, dried at 100°C, sublimed and weighed (yield: 5.076g, 86.6%). The washing was added to the filtrate. The whole volume of filtrate was then hydrolyzed using sodium hydroxide solution which was added drop-wise with continuous stirring until complete precipitation of the black magnetite was achieved (pH 9 to 11). The set up was then left to settle, filtered, washed with distilled water, dried at 250°C and weighed (yield: 9.2g, 99.0%). The final filtrate was left to evaporate at room temperature and the sodium chloride was collected in portions (yield: 5.7, 81%).

The same procedure was repeated using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a precursor. 27.03g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 150.0 ml distilled water was reacted with 5.533g (0.033 mol) KI aqueous solution. Iodine yield was 3.15g, 75.53%. Magnetite was precipitated from three 50.0 ml portions of the filtrate. The average yield was 1.40g, 91.61%.

The yield of magnetite from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ precursor was low (52.8%) when a 3Fe (III): 1.0 KI mole ratio was used. Increasing the ratio to 1:1.325 yielded a 97.0% I_2 and a 96.85% Fe_3O_4 .

Results and Discussion

Instead of using two iron precursors, that is Fe (III) and Fe (II) mixed in a 2:1 mole ratio for the preparation of magnetite, one can start with only an aqueous iron (III) salt solution and reduce it by potassium iodide to maintain the appropriate mole ratio according to Equation (7):



Thereafter, filtering out the iodine precipitate and then hydrolyzing the filtrate by 25% ammonium or sodium hydroxide solution at pH 9 to 11 were used to obtain black magnetite nanoparticles. The percentage yield of magnetite and iodine was 99 and 86%, respectively.

This innovative method for the preparation of magnetite is economical and green, achieving a high selectivity and atom economy percents [27]. Equations (8) and (9) imply that both magnetite and iodine are desired products.

$$\% \text{ selectivity} = 100 \times (9.2 + 5.076) / (19.46 + 6.584) = 54.78 \% \quad (8)$$

$$\% \text{ atom economy} = 100 \times (485.35 + 126.9) / (487.05 + 165.8) = 93.78 \% \quad (9)$$

The FTIR spectrum of the as-synthesized magnetite from anhydrous FeCl_3 (Figure 1) exhibited vibrational bands at 634 sh., 582 s, 397 m cm^{-1} characteristic of magnetite [3,28,29]. The intense band at 582 cm^{-1} could be assigned to the IR active T_{1u} mode corresponding to the vibration of the $\text{Fe}^{2+}-\text{O}^{2-}$ functional group. The splitting-up peak at 634 cm^{-1} is due to the symmetry degeneration on octahedral B sites [28]. Rowan and Patterson [30] have reported that for monoclinic unit cell at low temperature, the IR modes in the $\text{Fe}^{2+}-\text{O}^{2-}$ stretching vibrational band would be induced as obvious split pairs for fields along the x and y directions.

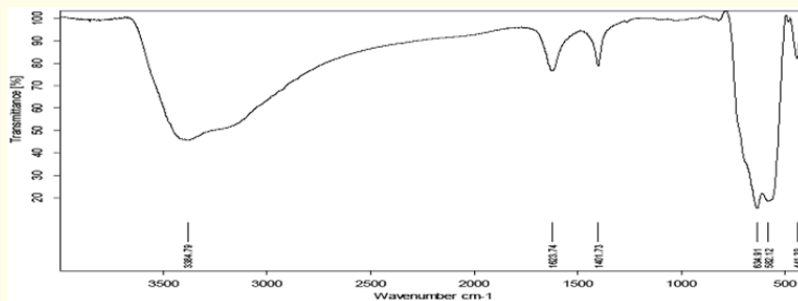


Figure 1: FTIR spectrum of the as-synthesized magnetite.

The EDS intensity peaks (Figure 2) show the exact iron percent in Fe_3O_4 . The Cu signals were from the Cu grid. No other signal was detected within the detection limits of EDS which confirms the purity of the Fe_3O_4 nanoparticles.

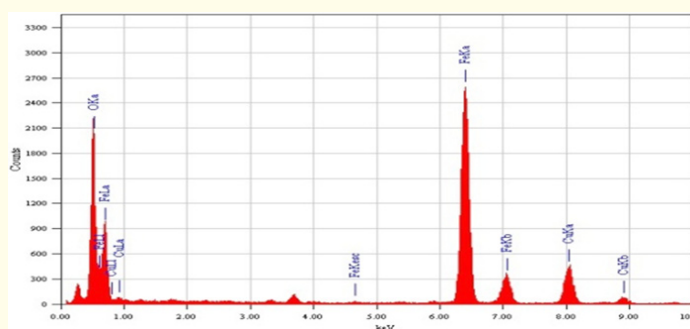


Figure 2: EDS pattern of the as-synthesized magnetite.

The crystallinity of the magnetite sample was investigated by XRD as shown in Figure 3. The results show that the sample has six peaks at 2θ of 30.36, 35.74, 43.52, 53.95, 57.34 and 63.0° representing the corresponding indices of (220), (311), (400), (422), (511), and (440) respectively [3,25].

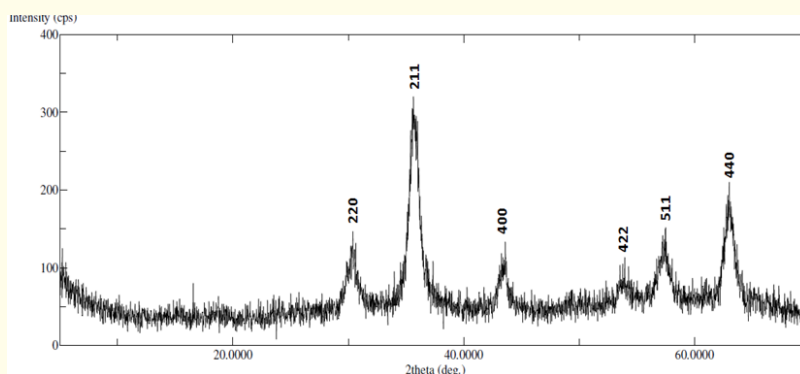


Figure 3: XRD diffraction pattern of the as-synthesized magnetite.

The crystal system is cubic with Z value of 8.0, $a = b = c = 8.3199 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ belonging to space group Fd-3m. A typical scanning electron microscopic (SEM) image of the as-synthesized iron oxide nanoparticles is shown in Figure 4. It is evident from the picture that the particles are in a nano scale.

TEM image (Figure 5) of the synthesized magnetite indicates the formation of nanocubes and nanorods composite.

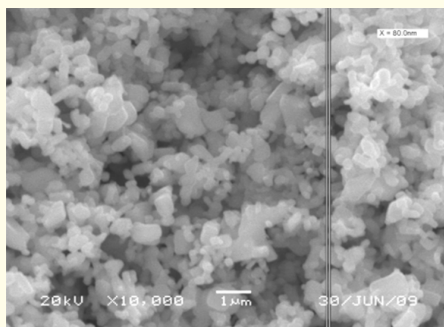


Figure 4: SEM image of the synthesized magnetite.

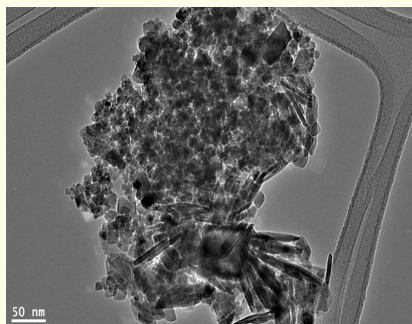


Figure 5: TEM image of the as-synthesized magnetite.

The selected area electron diffraction (SAED) pattern of the as-synthesized iron oxide is shown in Figure 6a. The high resolution TEM image of a single iron oxide cube (Figure 6b) shows lattice fringes with an interfringe distance of 0.292 nm, which is close to the interplane distance (220) of the planes in the cubic spinel structured iron oxide [25].

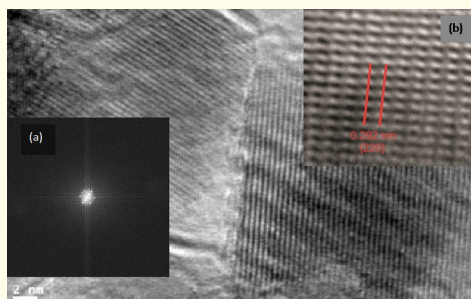


Figure 6: HRTEM image of the as-synthesized Fe₃O₄: (a) SAED pattern and (b) Lattice fringes.

A more monodispersed magnetite nanoparticles could be obtained by hydrolyzing a salty iron solution as is shown by TEM, SAED and HRTEM images, (Figure 7, 8, & 9, respectively).

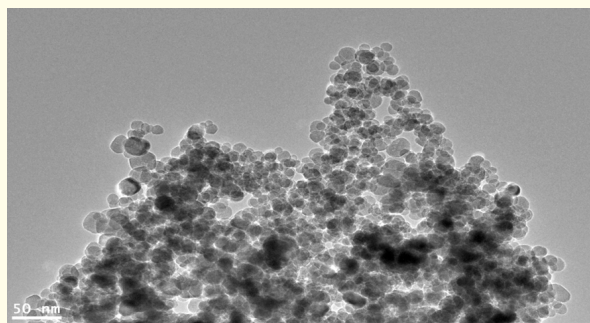


Figure 7: TEM image of magnetite nanoparticles precipitated from salty iron solution.

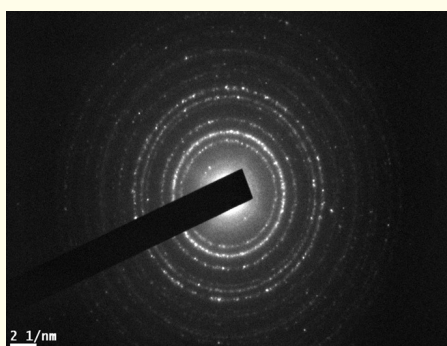


Figure 8: SAED image of magnetite nanoparticles precipitated from salty iron solution.

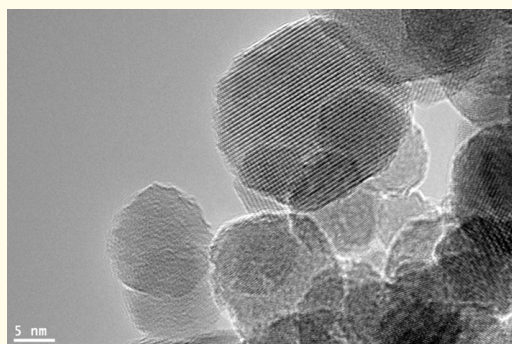


Figure 9: Interfringes image of magnetite nanoparticles precipitated from salty iron solution.

Information of the mean size and standard deviation (SD) was calculated from measurements of the nano cubes and nanorods in random fields of view and presented in Figure10. The mean \pm SD of the nanocubes was 7.8 ± 0.05 nm while the mean \pm SD of the nanorods was 6.3 ± 0.2 nm in diameter and 46.2 ± 0.9 nm in length.

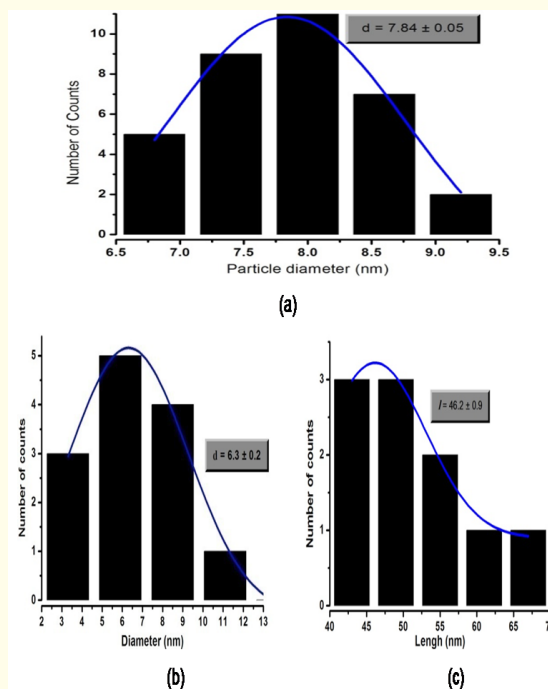


Figure 10: Mean size and standard deviation of Fe_3O_4 nano cubes (a), and Fe_3O_4 nano rod (b and c).

The iodine crystals obtained by subliming the drude product is shown by figure 11.

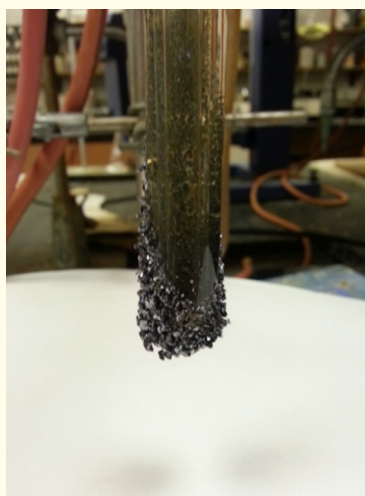


Figure 11: Picture of sublimed iodine crystals.

Liquid nitrogen temperature (77K) and room temperature (300K) ^{57}Fe Mossbauer spectra of one magnetite-loaded PVA dry hydrogel sample are presented in Figure 12(a,b). The 77K recorded spectrum, Figure 12 (a), is similar to that of an assembly of 8-to 10-nm noninteracting magnetite particles published by Morup., *et al.* [31] and Szabo., *et al.* [32]. The RT ^{57}Fe Mossbauer spectrum consists of two sextets with isomer shifts of 0.15 mm/s and a hyperfine field of 48.6T for Fe^{3+} in the A sites and 0.56 mm/s and a hyperfine field of 45.7T for the $\text{Fe}^{2.5+}$ average valence on the B sites [33]. A quadrupole splitting of 0.00 and -0.01 mm/s is indicative of cubic symmetry. The absence of a paramagnetic component indicates that the transition to paramagnet occurs above 300K.

Detailed ^{57}Fe Mossbauer Effect study will be conducted and published elsewhere.

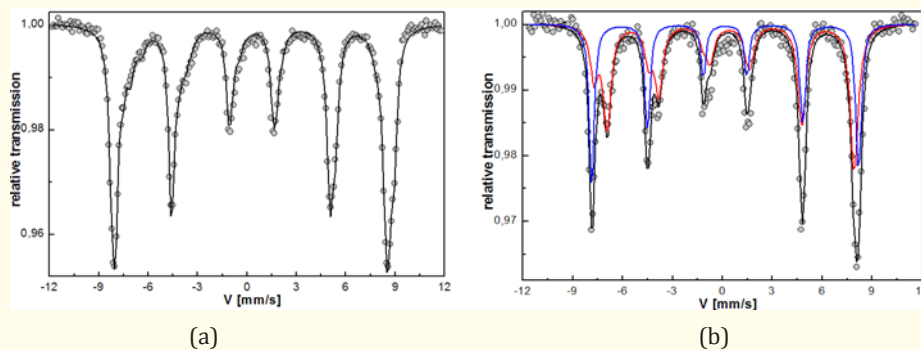


Figure 12: Mössbauer spectra of a disk-shaped dried ferrogel at 77K (a) and 300K (b).

Conclusion

In this paper, we provided a green and economical process by which three economically feasible products are obtained, viz, magnetite nanoparticles, iodine and table salts by one reaction. Further, only one Fe (III) salt is used instead of two as in prior arts. The yield of all three products is quantitative achieving a high atom economy and selectivity. The size and morphology of the magnetite nanoparticles could be manipulated by hydrolyzing salty prepared iron solutions. A 100% pure iodine crystals are obtained by subliming the crude product. Table salt is then obtained by slow crystallization of the filtrate.

Bibliography

1. Raj K., *et al.* Magn. Mater., 85 (1990): 233.
2. Xie J., *et al.* "Ultrasmall c(RGDyK)-Coated Fe_3O_4 Nanoparticles and Their Specific Targeting to Integrin $\alpha\text{v}\beta_3$ -Rich Tumor Cells". *Journal of the American Chemical Society* 130.24 (2008): 7542-7543.
3. Cornwell RM and Schwertmann U. "The Iron Oxides". Structure, Properties, Reactions, Occurrences and Uses. Sed. Edition, Wiley-VCHGmbH&Co. (2003).
4. David I and Welch AJE. Trans. Faraday Soc. 52 (1956): 1642-1650.
5. Schikorr, GZ., *Electrochemistry* 35 (1929): 65.
6. Regazzoni AE., *et al.* A. J. G *Journal of Inorganic and Nuclear Chemistry* 43(1981): 1481-1493.
7. Ardizzone S and Formaro L. Mat. Chem.Phys. 8 (1983): 125-133.
8. Blesa MA and Maroto. A. J. G., *Journal of Chemical Physics* 83 (1986): 757-764.
9. Booy M and Swaddle TW. "Hydrothermal preparation of magnetite from iron chelates". *Canadian Journal of Chemistry* 56.3 (1978): 402-403.
10. Pinheiro E A., *et al.* CRS study, Langmuir. 3 (1987): 445-448.

11. Sarel S., *et al.* 28(1989): 4187-4189.
12. Robl R. "Über ferromagnetische Eisenoxyde". *Angewandte Chemie* 70.12 (1958): 367-371.
13. Kominami H., *et al.* "Synthesis of Microcrystalline Hematite and Magnetite in Organic Solvents and Effect of a Small Amount of Water in the Solvents". *Journal of American Ceramic Society* 82.7 (1999):1937-1940.
14. Laux J IG., *Farbenindustrie DE* (1925): 463-773.
15. Michael B., *et al.* "Magnetic Nanoparticles is having biochemical activity". Method for the production there of and their use. US Patent 767.6 (2004): 635.
16. Shen H. "Process for preparing dispersive nano Fe₃O₄ particles". Publication number: CN 1365951 (2002).
17. Yoshito N., *et al.* "Method for preparing magnetite magnetic powder". US Patent 4436681 (1984).
18. Tomio H and Hiroyuki S. "Magnetite particles". US Patent 5885740 (1999).
19. Shouheng S. "Synthesis of magnetite nanoparticles and the process of forming Fe-based". US Patent 6962685 17 (2002).
20. Maurice G., *et al.* "Process for the production of magnetite spheres with an arc heater". US Patent 4071588 (1978).
21. Naoyoshi M and Kenzo H. "Black ultrafine magnetite particles and process for preparing the same". US Patent 6083476 (2000).
22. Hui C., *et al.* "Large-Scale Fe₃O₄ Nanoparticles Soluble in Water Synthesized by a Facile Method". *Journal of Physical Chemistry* 112.30 (2008): 11336-11339.
23. Fried T., *et al.* "Ordered Two-Dimensional Arrays of Ferrite Nanoparticles". *Advanced Materials* 13.15 (2001): 1158.
24. Sun S and Zeng H. "Size-Controlled Synthesis of Magnetite Nanoparticles". *Journal of the American Chemical Society* 124.28 (2002): 8204-8205.
25. Xu Z., *et al.* "Organic phase synthesis of monodisperse iron oxide nanocrystals using iron chloride as precursor". *Nanoscale* 2 (2010): 1027-1032.
26. Khalil MI. "Process for preparing magnetite (Fe₃O₄) and derivatives thereof". (2012) EP 2 505 558 A 1.
27. Lancaster M. *Green Chemistry. An Introduction Text*, Royal Society of Chemistry, Thomas Graham House, (2002).
28. Zheng L., *et al.* "First-order metal-insulator transition and infrared identification of shape-controlled magnetite nanocrystals". *Nanotechnology* 22.48 (2011): 485706.
29. Liese HC. *American Mineral*. 52 (1967): 1198-1205.
30. Rowan AD and Patterson C H. "Hybrid density functional theory applied to magnetite: Crystal structure, charge order, and phonons". *Physical Review B* 79 (2009): 205103.
31. Morup S., *et al.* "Magnetic Microcrystals in Application of Mössbauer Spectroscopy". Cohen, R. L., Ed 2 (1980): 1.
32. Szabó D., *et al.* "Magnetic and Mössbauer Studies of Magnetite-Loaded Polyvinyl Alcohol Hydrogels". *Journal of Colloid and Interface Science* 221.2 (2000): 166-172.
33. Džési I., *et al.* "Phase transition in nanomagnetite". *Journal of Applied Physics* 103 (2008): 104312.

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