Analysis of nanorice structure formed by hydrolysis reaction of FeCl3 with KH2PO4

Armstrong, Oliver; Thomas, P. John

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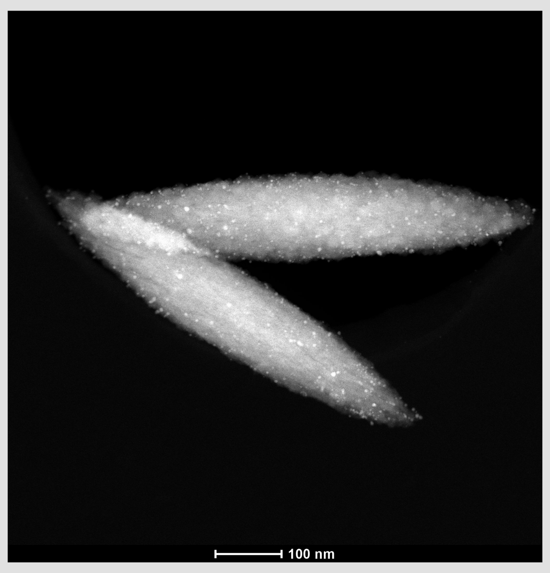
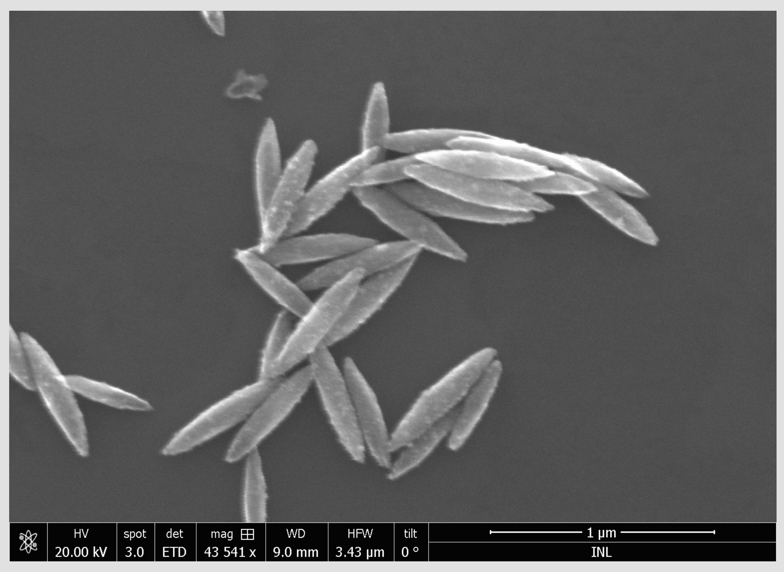
Analysis of nanorice structure formed by hydrolysis reaction of $FeCl_3$ with KH_2PO_4.

Oliver L. Armstrong, P. John Thomas

chue20@bangor.ac.uk School of Chemistry

Bangor University, Bangor, Gwynedd, Wales, UK LL57 2UW





Forced Hydrolysis Process

The method of producing hematite in this process involves the precursor $FeCl_3$ being dissolved in aqueous solutions, with a small addition of KH_2PO_4 and heating at 100°C, for between 12-72 hours.[1] The length of time heating correlates closely with both the shape of the hematite particles produced and their aspect ratio. The process proceeds by a forced hydrolysis of Fe^{3+} to form an orthophosphate group and the hematite product.[2] The use of KH_2PO_4 in this method is important to ensure the morphological structure of the formed particles as a nanorice elliptical shape.[3]

Scheme 1. Formation Mechanism of α-Fe_2O_3

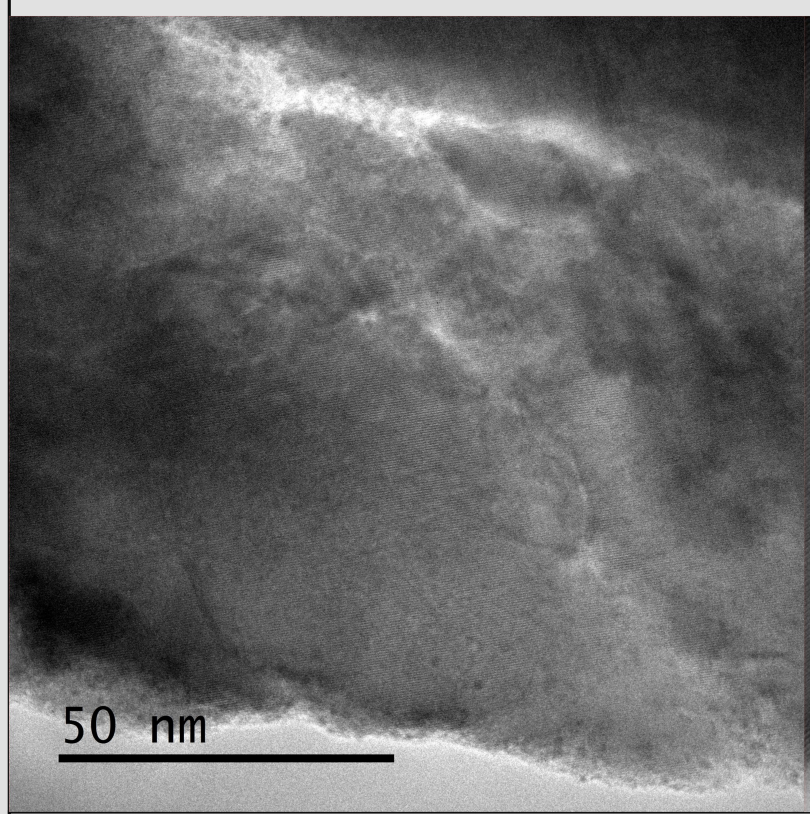
$$FeCl_3 + 6\,H_2O \rightarrow Fe(H_2O)_6^{3+} + 3\,Cl^-$$

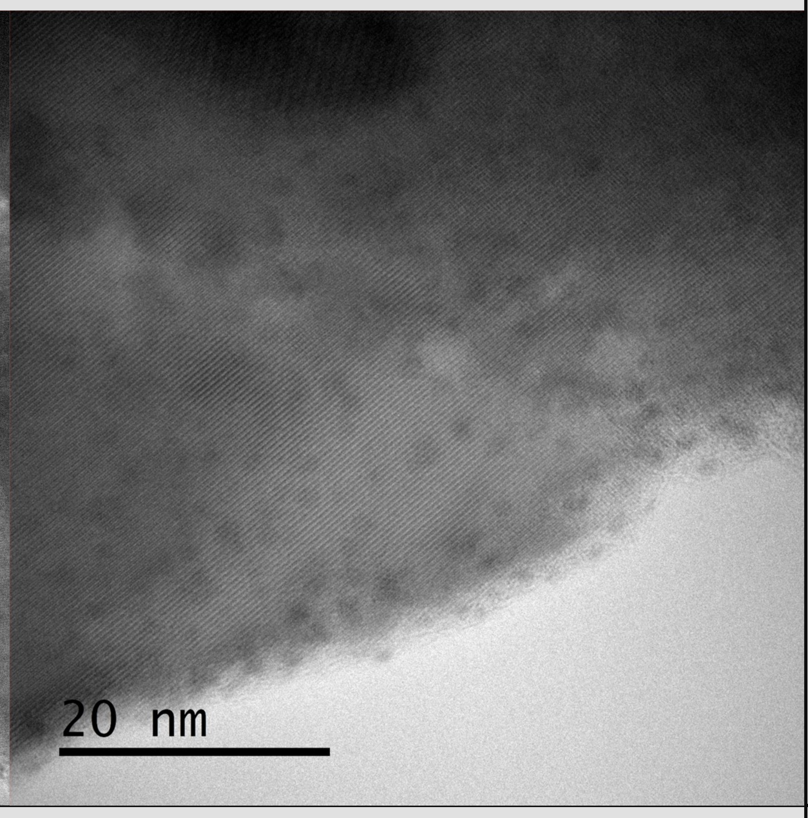
$$Fe(H_2O)_6^{3+} \rightarrow FeOOH + 3\,H^+ + 4\,H_2O$$

$$2\,FeOOH \rightarrow \alpha\text{-}Fe_2O_3 + 2\,H_2O$$

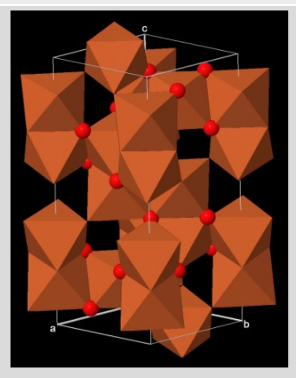
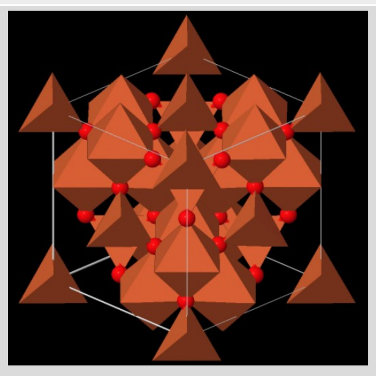
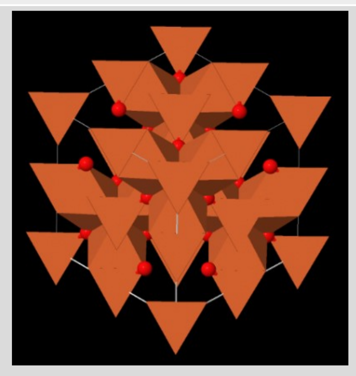
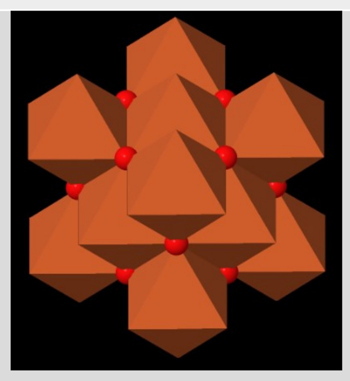
TEM studies

HRTEM images have confirmed to us the nanorice shape of our formed hematite particles. Some HRTEM images have also confirmed to us that these particles are of a single crystal structure. The lattice constants have been found to be in close agreement to calculated values for hematite, with crystal planes (121), (011), (111) and (112) being identified. We also attained EDX maps of the nanorice, confirming the particles were indeed a mix of iron and oxygen. The particles were found to be 500nm in length and around 100nm width at widest point, giving an aspect ratio of 5. Very little variation in size and shape of particles was observed between batches.





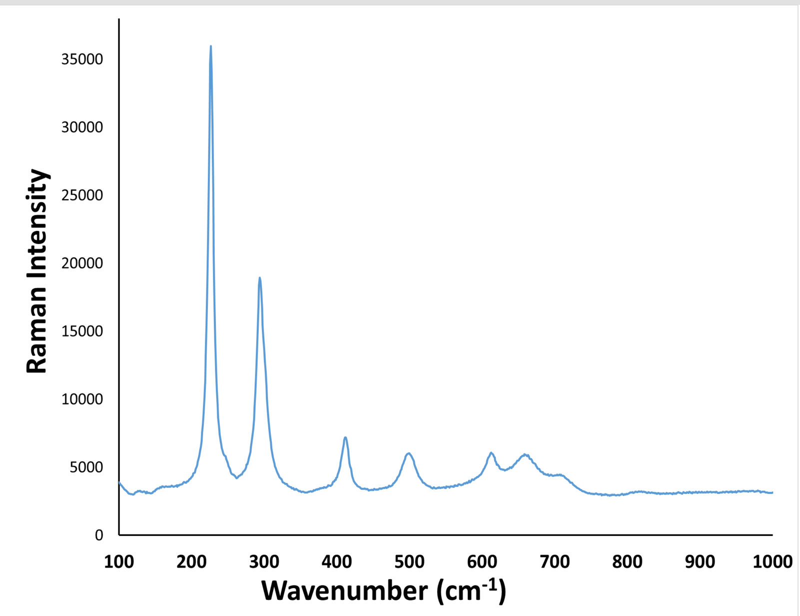
Structural Comments

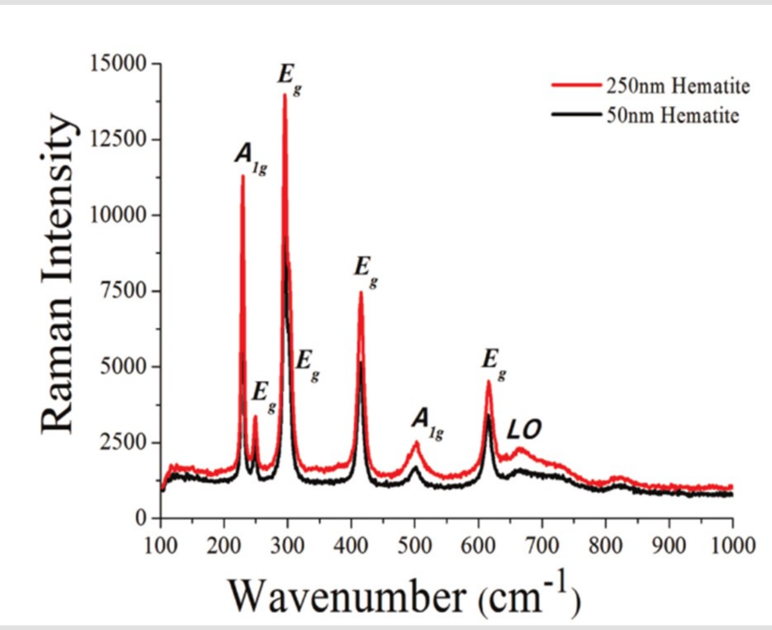
Name	Hematite	Maghemite	Magnetite	Wüstite
Chemical Formula	α-Fe_2O_3	γ-Fe_2O_3	Fe_3O_4	FeO
Oxidation state	Iron $^{3+}$	Iron $^{3+}$	Iron $^{2+}$ and Iron $^{3+}$	Iron $^{2+}$
Cell Structure				
Space Group	R -3 c H	P $4_1 2_1$ 2 [5]	F d 3 m	F m 3 m
Bulk magnetism	Weakly ferro/ anti-ferromagnetic	Ferrimagnetic	Ferrimagnetic	Anti-ferromagnetic

As can be seen just slight changes in the positioning and number of Iron and Oxygen atoms in the unit cell results in changes in the geometry, properties and valency of the atoms. All of these examples are based on a close packed Oxygen anion lattice with Iron cations located in the interstitial sites.

Raman Spectroscopy

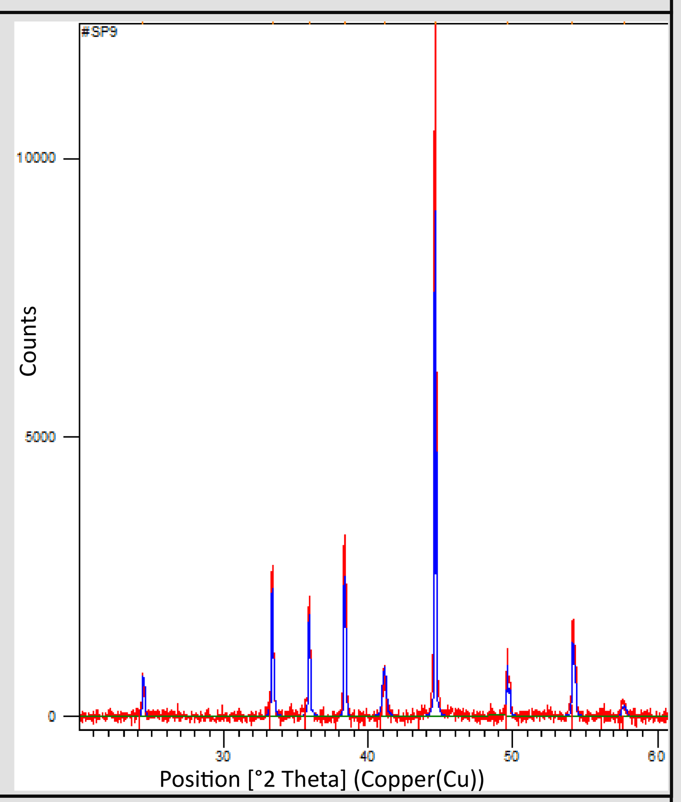
Our produced iron oxide particles have been analysed by raman spectroscopy. When comparing our spectras against published spectras, both calculated and observed, there is a close fit for that of hematite confirming our produced particles have a chemical structure of α-Fe_2O_3.[4] This will have implications to properties of the particles such as density, hardness and magnetism.





XRD studies

Our diffractograms are found to be similar to published data of hematite, with key peaks found at certain degree points. XRD data builds a definite crystal structure of the sample by measuring electron density of the crystal structure at a range of angles. The peaks found at 24.4, 33.3, 35.9, 41.1, 49.6 and 54.2 degrees indicate a close correlation to published data.[6] The radiation source used was Copper Kα with a wavelength of 1.541Å.



Analysis Conclusions

In conclusion the nanorice shaped Fe_xO_x particles have been studied by a variety of techniques, which all confirm the crystal structure to be that of hematite. We have proven the high morphological control of the method with close to monodisperse populations of nanorice of 500nm in length. A combination of these resolved properties means we can have highly controlled dispersions of magnetic particles.

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