

# The effect of phosphonate-based growth modifiers on the morphology of hematite nanoparticles formed *via* acid hydrolysis of ferric chloride solutions

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Paper

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The effect of organic phosphonate-based additives on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) crystallization *via* the forced hydrolysis of ferric chloride solutions has been studied using a range of additives containing 2, 3 or 4 pendant phosphonate groups. The hydrolysis reactions were carried out at pH 1.1 with an iron concentration of 0.01 mol L<sup>-1</sup>, and with Fe : additive ratios ranging from >8000 : 1 down to 200 : 1. In the absence of additive, the hematite particles are very uniform rhombic single crystals, with an average length of  $\approx$ 100 nm. In the presence of phosphonates the particles become hexagonal, with the additives acting by inhibiting growth at (2 $\bar{1}$ 4) faces. At Fe : additive ratios lower than about 200 : 1, hematite formation is completely inhibited. Our results are consistent with a mechanism in which the akaganéite and hematite phases may both precipitate from the ferric chloride solution, with akaganéite apparently forming more rapidly than hematite. Inhibition of hematite formation by addition of the phosphonate additive can lead to  $\beta$ -FeOOH (akaganéite) being the dominant product phase, provided the concentration of Fe<sup>3+</sup> in solution is above the equilibrium solubility of the akaganéite phase.

## Introduction

Specific control of size and shape is one of the prime challenges in the synthesis of nanoparticles, since such characteristics at the individual particle level are known to play an important role in determining the properties of bulk dispersions and composites. Careful selection of reaction conditions, reagent concentrations and mixing regimes often provides a degree of size and shape control in nanoparticle precipitation reactions, and a considerable amount of recent research has been devoted to developing such methods.<sup>1,2</sup> A more advanced goal in nanoparticle synthesis, however, is to exploit chemical additives, adsorbed species or template materials to control the crystal growth of nanoparticles and thus direct the formation of specific phases and crystal morphologies.

Iron oxide particles can be prepared in various morphologies *via* the forced hydrolysis of ferric chloride solutions, with careful control of reaction conditions providing highly uniform dispersions.<sup>3-5</sup> Moderate concentrations of FeCl<sub>3</sub> have been shown to yield spherical, cubic or ellipsoidal hematite particles of micron dimensions, while rhombohedral single-crystals of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite), of the order of tens of nanometers in diameter, are formed in solutions of low FeCl<sub>3</sub> concentration (<0.02 M) and pH of about 1.5.<sup>6</sup> The presence of phosphate has been shown to have a strong influence on the morphology of hematite particles grown in these systems, with only small amounts of this anion directing an ellipsoidal habit on the hematite particles.<sup>7,8</sup> This change in morphology has been shown to be caused by the binding of phosphate to crystal faces parallel to the hematite *c*-axis, thus limiting crystal growth to the *c*-direction. The crystal faces concerned have until now, not been precisely identified.

Given that the phosphate ion is known to adsorb strongly to iron oxide surfaces, and that it has been shown to affect the morphology of iron oxide particles, we have sought to

investigate the potential for morphological control of iron oxide nanoparticles by employing a range of phosphonate-based molecules. The effect of organic phosphonate-based additives on the forced hydrolysis of ferric chloride solutions has been studied by Reeves and Mann,<sup>9</sup> but these molecules have otherwise received little attention in regard to iron oxide precipitation, and the phosphonate additives used in this study have not previously been investigated as modifiers of hematite crystal growth. Our group has studied the effects of a range of phosphonate molecules on the crystal growth of calcite, and barium sulfate systems, using systematic variation of molecular structure of the phosphonate additives.<sup>10-12</sup> In this paper, we describe the effects of phosphonate additives containing 2, 3 or 4 pendant phosphonate groups, on the precipitation of hematite *via* forced hydrolysis of FeCl<sub>3</sub> solutions.

## Experimental

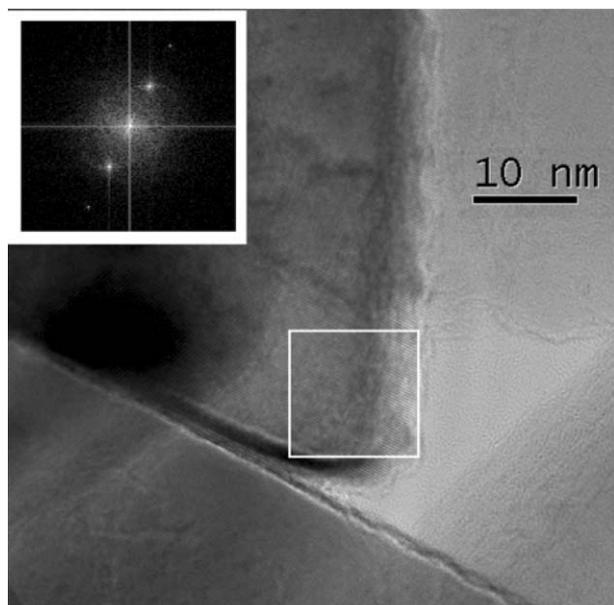
### Phosphonate additives

The phosphonate-based additives, the structures of which are shown in Fig. 1, are for ease of reference designated by abbreviated names as follows: MNDP = methyl nitrilo dimethylenephosphonic acid; NTMP = nitrilo trimethylenephosphonic acid; EDTP = ethylenediamine tetraphosphonic acid; DOTP = tetraazocyclododecane tetramethylene phosphonic acid; EDTP was Aldrich AR Grade. Other phosphonate additives were synthesised in-house according to published methods.<sup>13,14</sup>

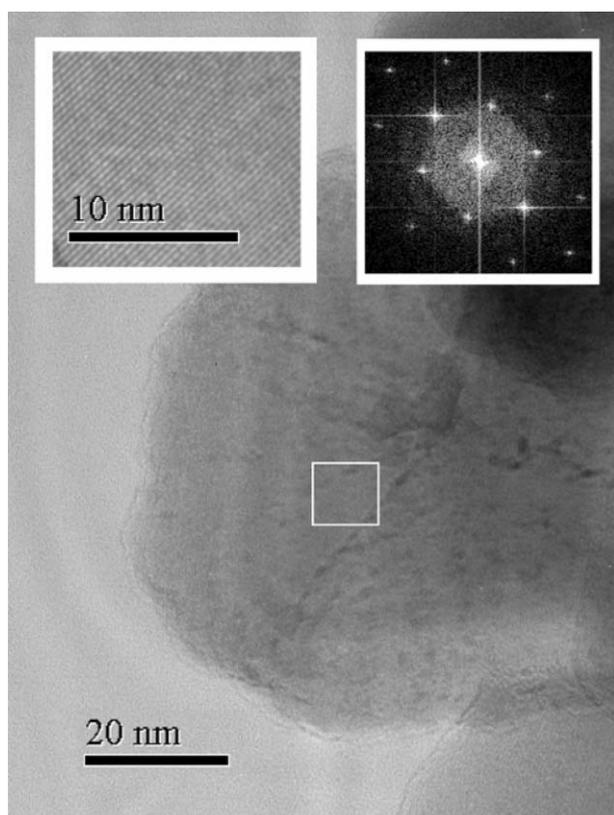
### Iron oxide nanoparticles

In a typical experiment, 50 ml of 0.2 mol L<sup>-1</sup> FeCl<sub>3</sub> solution and 50 ml of 0.04 M HCl were mixed at room temperature, then 900 ml of hot deionized water (>90 °C) was added. The



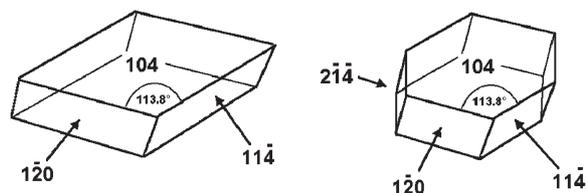


**Fig. 3** High resolution image of the edge of a rhombic hematite particle formed in the absence of any additive, showing lattice fringes attributed to (104) lattice planes. Inset: Fourier transform of the section of the image shown by the white square.



**Fig. 4** Hematite particle formed in the presence of 0.5 ppm EDTP. Inset top left: high resolution image of the region shown by the white box. Inset top right: Fourier transform of this high resolution image.

*d*-spacings obtained from the Fourier transform of the high resolution image shown in Fig. 4, the other faces of the rhombic crystals can be indexed as shown in Fig. 5. This morphology is consistent with the observed angles between the crystal faces, *i.e.* the expected angle between (120) and (114) planes is 113.8°. Our assignment of the (214) plane as the active site for phosphonate binding is more speculative however, since the particles formed with higher additive concentrations have



**Fig. 5** Hematite morphologies. In the absence of any additive (left), and in the presence of phosphonate (right).

rather roughened surfaces on this face, making it difficult to accurately determine the angles relative to other crystal planes.

On the basis of reasonable estimates however, the (214) face seems the most likely candidate. Although the sites of phosphate (and phosphonate) binding on hematite have been described previously in more general terms, this is the first time a specific crystal face has been identified as the site of additive binding.

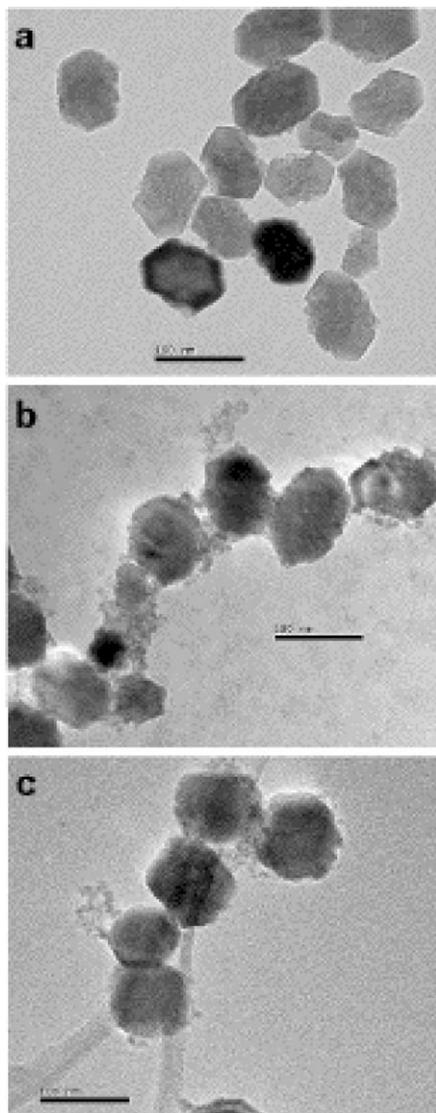
All of the phosphonates used in this study appear to act similarly in binding at the intersection of (120) and (114) faces, resulting in hexagonal particles with two opposite faces having roughened surfaces. The effects of MNDP, NTMP and DOTP can be seen in Fig. 6. MNDP is a di-phosphonate additive, while NTMP contains three pendant phosphonate groups, and DOTP four. In the particles precipitated in the presence of MNDP and NTMP, the roughened (214) face appears to be well developed and the particles have the form of “flattened” or elongated hexagons. When EDTP is employed at a similar concentration, (*cf.* Fig. 2) the particles have a more regular hexagonal shape and the (214) faces are smaller. This is also the case when DOTP is employed. These observations suggest that MNDP and NTMP may be more potent growth modifiers than EDTP and DOTP, although it must be conceded that the effect has not been quantified here, and further work will be needed to fully characterize the relative inhibitory effects of the four additives.

#### Mechanism of hematite precipitation

In samples precipitated in the presence of MNDP and DOTP, the hexagonal particles were associated with a considerable amount of much smaller, poorly-crystalline material, made up of approximately spherical particles only a few nanometres in diameter. The nature and particle size of this material suggests the hydrous ferric oxide, ferrihydrite. Ferrihydrite, which is given the approximate formula  $\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , is generally the first product to form from ferric ion hydrolysis in acid media.<sup>16,17</sup> Sugimoto and Muramatsu,<sup>4</sup> in their study of the mechanism of hematite formation, did not observe evidence of ferrihydrite precursors, but Kan *et al.*<sup>6</sup> reported the formation of nanometer-sized amorphous spheres in samples prepared under conditions very similar to those of our experiments.

It has been reported by a number of previous workers<sup>4-6,15</sup> that  $\beta\text{-FeOOH}$  (akaganéite) is an intermediate phase in formation of hematite *via* acid hydrolysis of ferric chloride, with the conversion to  $\alpha\text{-Fe}_2\text{O}_3$  occurring *via* re-dissolution of the  $\beta\text{-FeOOH}$  particles and subsequent nucleation and growth of hematite from soluble iron hydroxide species. However, powder XRD spectra of the hydrolysis products obtained in this study showed no peaks attributable to akaganéite, but rather only hematite reflections were observed.† In fact we have seen no evidence of the akaganéite phase in any of our

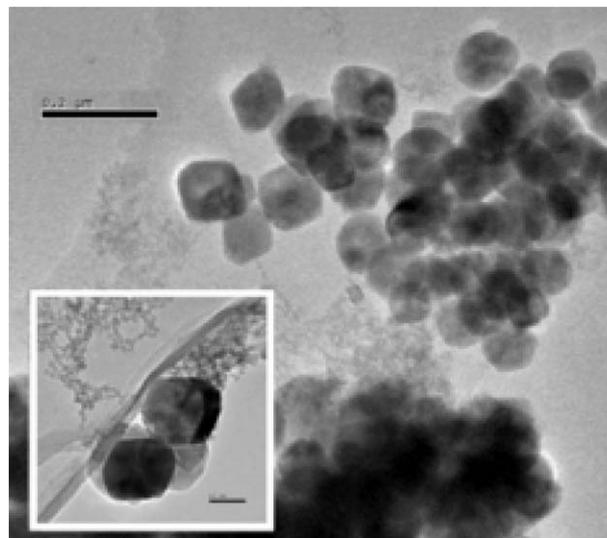
† Due to its low crystallinity, 2-line ferrihydrite is difficult to detect in XRD spectra unless present in quantities greater than 10% by weight,<sup>17</sup> so we can conclude that although there is certainly some ferrihydrite present in these samples it probably constitutes only a few weight percent of the material.



**Fig. 6** Hematite nanoparticles formed in the presence of 5 ppm a) MNDP, b) NTMP and c) DOTP. Size bars = 100 nm.

experiments carried out at  $\text{Fe}^{3+}$  concentrations of  $0.01 \text{ mol L}^{-1}$  or less. This is probably due to the fact that at a concentration of  $0.01 \text{ mol L}^{-1}$  in  $\text{Fe}^{3+}$ , the system is below the solubility limit for akaganéite.<sup>1</sup> Thus we can conclude that at low  $\text{Fe}^{3+}$  concentrations, the pathway to hematite formation involves initial precipitation of ferrihydrite, followed by dissolution and reprecipitation to form hematite. In contrast, at higher concentrations of ferric chloride, the akaganéite phase forms as a side product in the pathway to hematite formation, and thus inhibition of hematite nucleation and/or growth can result in akaganéite being isolated as the major product of the hydrolysis reaction.

Most of the reported work on the ferric chloride system has been carried out at  $\text{Fe}^{3+}$  concentrations greater than  $0.01 \text{ mol L}^{-1}$ ,<sup>1,2</sup> and in this concentration range, particles prepared in the absence of any additive are roughly cubic crystals of 1–2  $\mu\text{m}$  in size. The particle morphology is, however, sensitive to the total chloride concentration and thus, at lower concentrations of  $\text{FeCl}_3$ , well-defined rhombohedral particles are obtained, with particle diameters typically in the range of 40–100 nm. The effect of the chloride ion on particle morphology is demonstrated in Fig. 7, which shows TEM images of the rounded cubic particles obtained when the chloride concentration is raised to  $0.09 \text{ mol L}^{-1}$  by the addition of NaCl, while other reagents were maintained at the control conditions. The particles are also highly aggregated, and are



**Fig. 7** Hematite particles formed in the absence of any additive, but with increased chloride ion concentration ( $[\text{Fe}^{3+}] = 0.01 \text{ mol L}^{-1}$ ,  $[\text{Cl}^-] = 0.09 \text{ mol L}^{-1}$ ). Inset: higher magnification image showing ferrihydrite particles surrounding larger hematite rhombs. Size bars main picture = 200 nm, inset = 50 nm.

associated with ferrihydrite, which to some extent appears to bind the aggregates together.

As mentioned earlier, a further effect of high chloride concentrations is to stabilise the  $\beta\text{-FeOOH}$  (akaganéite) phase.<sup>5,6,15</sup> Reeves and Mann studied the effects of organic phosphonates on the acid hydrolysis of ferric chloride solutions at  $\text{Fe}^{3+}$  concentrations of  $0.02 \text{ mol L}^{-1}$ , and with Fe : additive ratios considerably lower than we have employed here; that is to say, relatively higher concentrations of additive were employed. They found that in most cases, the hydrolysis reaction was completely inhibited and no precipitate was formed, but in the case of 1,2-ethylenediphosphonic acid, the product was exclusively akaganéite. Our own experiments on the effects of EDTP at higher  $\text{Fe}^{3+}$  concentrations are consistent with these observations. Solutions of ferric chloride ( $0.03 \text{ mol L}^{-1}$ ) aged for 48 hours in the absence of EDTP produced only hematite cubes, while the addition of EDTP led to the formation of inter-grown cubic particles associated with a considerable amount of rod-shaped akaganéite. With Fe : additive ratios lower than about 100 : 1, akaganéite was the only product observed after 48 hours at  $98^\circ\text{C}$ .

## Conclusions

The phosphonate additives examined in this study all show an inhibitory effect on the growth of hematite crystals formed *via* the acid hydrolysis of ferric chloride solutions. In the absence of the phosphonates, the hematite particles are uniform rhombic crystals with an average length of about 100 nm, and the basal plane of these rhombic particles is the (104) face. The addition of small amounts of phosphonate leads to a hexagonal morphology, probably caused by additive binding at  $(2\bar{1}4)$  planes. In the case of EDTP, hematite formation is completely inhibited at concentrations greater than 20 ppm ( $0.052 \text{ mmol L}^{-1}$ ). Thus, the morphological control provided by these additives seems to be quite specific, involving selective binding of the additive to a particular crystal face. In general terms, the location of phosphonates and phosphate ion binding on hematite has been described previously as “crystal faces parallel to the  $c$ -axis”. This is the first time however, that a specific crystal face has been identified as the site of additive binding on hematite. Indexing of the crystal and identification of the additive binding site is important, since such information may provide clues as to the precise mode of

interaction of the additive molecules with hematite surface groups. The underlying reasons for selectivity may arise from the geometry of pendant phosphonate groups relative to the orientation of atoms at the (2 $\bar{1}$ 4) surface, and molecular modelling of phosphonate interactions with hematite surfaces may provide further information to complement the results described here.

The comparison between experiments carried out at Fe<sup>3+</sup> concentrations of 0.01 mol L<sup>-1</sup> and those involving higher concentrations of ferric chloride provide an important insight into the mechanism of ferric ion hydrolysis in acid solutions. At higher Fe<sup>3+</sup> concentrations, inhibition of hematite formation results in akaganéite precipitating as the dominant phase. This is consistent with a mechanism in which the akaganéite and hematite phases may both precipitate from the ferric chloride solution, with akaganéite apparently forming more rapidly than hematite. Given the greater solubility of akaganéite, however,<sup>16</sup> the amount of this phase present in the mixture decreases with time as hematite forms and the overall Fe<sup>3+</sup> concentration decreases below the equilibrium solubility of akaganéite. At low initial concentrations of Fe<sup>3+</sup> (*i.e.* if the concentration is already below the limit for akaganéite precipitation) akaganéite is not observed, and hematite samples prepared in the presence of phosphonate additives can co-precipitate with ferrihydrite, which is a ubiquitous precursor to iron oxide formation.

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