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Growth kinetics evaluation of hydrothermally synthesised β-FeOOH nanorods

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Oriented attachment kinetic, Empirical correlation,

Abstract:

Based on the proposition that a quantitative and qualitative relationship between alcohol surface tension and particle growth exists, the effect of four different organic solvents on the growth kinetics of β-FeOOH nanorods have been evaluated in this study. Two-stage growth of akaganeite nanorods have been observed in the presence of butanol and propanol as solvents. The first growth stage follows a typical power law representing Ostwald Ripening (OR) kinetic. The second stage of growth was found to be asymptotic. The second stage of growth was fitted by the Oriented Attachment (OA) kinetics. HRTEM images of the synthesized particles also showed crystallographically specific oriented attachment based growth of the particles. Signs of OA mechanism was not observed from the TEM images of the particles synthesised using ethanol and methanol as solvents. The rate constants for each kinetic was evaluated and the rate constant for OR kinetics, k_{OR}, was found to be significantly higher than the rate constant for OA kinetics, k_{OA}, under the reported conditions for the four different solvents used. The rate constants were related to the surface tension of alcohol. The established quantitative and qualitative relationship was also validated by an independent study. By correlating the surface tension of solvents with different process parameters a generalized correlation has been developed to predict β-FeOOH aspect ratios for the first time. This correlation takes three different process parameters in conjunction with the solvent surface tension to predict particle aspect ratios with acceptable confidence.

1. Introduction:

Nano materials with one dimensional (1D) crystal structure such as nanowires, nanotubes, nanorods and nanoribbons have unusual and captivating chemical and physical properties, such as photochemical, photophysical and electron transport properties [1]. Understanding of the factors that influences the crystal growth kinetics and microstructure development of nanocrystals is central to the control of nanoparticle properties. Ostwald ripening (OR) theory which is the classical crystal growth kinetics is customarily used to explain the diffusion-controlled crystal growth process, in which larger particles grow at the expense of smaller particles. OR crystal growth is typically described by the following power law [2]:

$$D = D_o + k(t)^{\left(\frac{1}{n}\right)} \qquad \text{Equation 1}$$

where, D, is the particle diameter, k, is the growth rate constant, t, is time and n is determined by the nature of the rate limiting step. But in recent years another significant mechanism termed “oriented attachment”, (OA), was brought into attention by Penn and Banfield in 1998 [3]. In this mechanism nanoparticles with common crystallographic orientations directly combine together to form larger ones. Compared with the classical atom/molecular-mediated crystallization pathway, the OA mechanism shows its specific characteristics and roles in the process of nanocrystal growth [3]. The evidence of OA based growth comes both from the interpretation of microstructure and the deviation of the growth kinetics from the OR model. OA growth does not follow Ostwald ripening kinetics [2]. The evolution of particle size is well described by the following expression [4]:

$$D = \frac{D_o\left(\sqrt[3]{2}kt + 1\right)}{\left(kt + 1\right)} \qquad \text{Equation 2}$$

where, D, is particle diameter, k, is rate constant and t, is time. Recent interests are more focused on the analysis of the role of OA mechanism rather than the comprehensive insight of the mechanism and kinetics. The inner complicacy of crystal growth and the occurrence of coexisting mechanisms lead to the difficulty and lack of understanding this growth process by the OA mechanism [3]. Only one work was conducted [4] in the literature where it was shown that addition of mercaptoethanol can isolate the growth stages during the hydrothermal synthesis of ZnS nanocrystal. However, growth kinetics of β-FeOOH nanoparticles has been sadly overlooked.

Table 1. TEM observation of OA mechanism during the growth of iron oxide nanoparticles

Author	**Year**	**Iron oxide phase**	**Morphology**
Penn et al.,11	2001	α-Fe_2O_3 and FeOOH	Rounded hematite particles Irregular feroxyhite plates
Niederberger et al.,12	2002	α-Fe_2O_3	Rounded hexagonal plate
Guyodo et al.,13	2003	α -FeOOH	nanorods
Nestrova et al.,14	2003	FeOOH	Various
Frandsen et al.,15	2005	α-Fe_2O_3	Chains
Penn et al.,16	2006	α-FeOOH	Nanorods

The application of alcohol in the synthesis of metal oxide nanoparticles can be found in the literature. Hematite nanoplates were synthesised using organic alcohols as solvents [5]. The authors reported that the thickness and diameter of the nanoplates can be finely tuned by the selective choice of solvent however detailed explanation was not presented to explain the reason behind it. Synthesis of α-Fe_2O_3 nanorods and tubes in the presence of butanol and different surfactants (L113B and SPAN 80) are also presented in the literature [1]. The synthesis of arrayed akaganeite nanorods and hexagram using ethanol as solvents are also found [6]. Application of alcohol was also observed in the literature during the synthesis of titania nano colloids [7]. Despite the wide applications of organic alcohol as solvents in the synthesis of metal oxide nanoparticle the role of alcohols on the crystal growth kinetics of these metal oxides have not been attempted to study. Akaganeite (β-FeOOH) has a hollandite-like crystal structure containing tunnel shaped cavities and has a wide range of applications [5]. Lithium can be intercalated and extracted freely in the tunnels (2X2) during discharge and charge processes thus making it a promising candidate for an electrode material in rechargeable batteries [6]. High catalytic activity of akaganeite for the hydro-processing of coal was also reported [5]. Adsorption and removal of arsenate and arsenite from aqueous solutions by akaganeite was also reported [8]. Akaganeite was synthesized and used as adsorbent to remove phosphate ions from phosphate-enriched seawater [9]. However, detailed growth kinetics of akaganeite nanorods is scarce in the literature despite of its numerous applications.

Surface tension plays an important role in controlling particle growth. A low enough solvent surface tension will promote the growth of 1D β-FeOOH nanorods [6,10]. However, no study was found in the literature that attempted to establish a relationship between solvent surface tension and particle growth despite the wide application of alcohol in the synthesis of metal oxide nanoparticles.

In the case of processes influenced by several variables, statistically designed experimental techniques have been shown to be a powerful tool for determining the effects of operational factors and their interactions. This method allows process optimization to be conducted effectively [27]. Despite of β-FeOOH nanoparticles many industrial and pure scientific applications there is no study that evaluates statistically the effect of each process variables on the growth of the nanorods. This type of study is necessary to identify the main variables to have better control over particle synthesis and growth from an engineering and /or commercial perspective.

In this paper we discuss the role of alcohols on the growth kinetics of akaganeite nanorods. A two stage crystal growth process during the hydrothermal coarsening of β-FeOOH nanorods with diameters of a few nanometres have been observed and reported. Based on the proposition that a quantitative relationship exists between particle growth and alcohol surface tension, a detailed evaluation of growth kinetics have been conducted, presented, and later validated by an independent study. This paper explains for the first time how statistically designed experiments can be used to predict β-FeOOH particle growth. A factorial trial method was used to evaluate the effect of each parameters and the effect of their interactions in the growth of β-FeOOH nanorods. A generalized correlation is developed by taking three different process parameters in conjunction with solvent surface tension to predict particle growth with acceptable confidence under the reported conditions.

1. Experimental

Analytical grade $FeCl_3.6H_2O$ and NH_4OH (B & M Scientific, Cape Town, R.S.A) were used as it is without any further purification. A certain amount of $FeCl_3.6H_2O$ was added to an equal amount of distilled water and alcohol to make up 0.05 M solution unless otherwise stated. Four different carbon chain length of alcohol (butanol, propanol, ethanol and methanol) was used for comparative purposes to evaluate the role of alcohol on the growth kinetics of the nanorods. To prevent the change in solution pH with the addition of different carbon chain length of alcohol the solution pH was always kept at constant at ~2. Ammonium hydroxide, NH_4OH, was used as a precipitating and pH controlling agent. The solution was placed in a 0.99 L Teflon-lined stainless steel pressure vessel with heating jacket consisting of a bottom heating plate and a side walled heating jacket. The reaction temperature was measured using a PT-100 dual channel thermocouple. The thermocouple was connected to a Gefran-800P controller. Standard reaction temperature of 100℃ and 2hr, was used unless stated otherwise. A heating rate of 1 ℃ / min was used to attain the desired temperature. Crystal growth was evaluated by performing a time evolution study. The synthesis time was varied from 2hr to 12hr to evaluate the crystal growth. The pressure vessel was cooled to room temperature naturally after the desired synthesis time. The supernatant liquid was decanted and the precipitated solids were collected. The solids obtained after each experiment was high speed centrifuged and finally was washed with a copious amount of ethanol. The wet solids were placed in a desiccator and left overnight to dry. A mechanism for the formation of the particles is proposed as the following:

$$\mathrm{FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl} \qquad \text{(a)}$$

$$\mathrm{Fe(OH)_3} \rightarrow \beta - \mathrm{FeOOH + H_2O} \qquad \text{(b)}$$

2.1 Characterization

The crystal structures of the synthesised products were determined using a Phillips PW 3830/40 Generator with a PW 3710 mpd control X-ray diffraction system with Cu-Kα radiation (λ = 1.506 Å). The surface morphology of the synthesised crystals was studied using a Tecnai TF20 thermionic TEM, equipped with a LaB6 filament and a Gatan GIF energy filter. Images were captured at 200 keV in bright field mode. Selected area electron diffraction (SAED) patterns were obtained using the smallest area aperture available. The average particle size was measured directly from the TEM images using image j © software. A minimum number of 200 particles were counted to have a better statistics. Counting of 90-100 particles are sufficient as suggested in literature [18].

3. Results and discussion

3.1 Dependence of β-FeOOH particle size on the carbon number present in the linear alkyl chain of the alcohol used as solvents

X-Ray diffraction (XRD) patterns of the synthesized standard samples are presented in Figure 1d. The measured XRD patterns matches very well with the standard diffraction patterns of monoclinic akaganeite without any signature of impurity (JCPDS card No. 42-1315). Transmission electron microscope image of the synthesised nanorods with corresponding d-spacing and SAED patterns is presented in Figure 1 a,b & c. Only pure crystalline akaganeite nanorods were synthesised in the case of all the four solvents used. The synthesis time did not have any effect on the phase of iron oxide nanoparticles. Several controlled experiments were performed to evaluate the effect of alcohol molecules on the growth of nanorods. The kinetics of the coarsening process under different solvent conditions were evaluated by measuring the size of the nanoparticles in both transversal and longitudinal directions. The mean particle size was estimated on the basis of measurements of a minimum number of 200 particles. The particle size increased with the increase in carbon number in the linear alkyl chain of alcohol as solvent. The variation of the full width at half maximum (FWHM) of {101}, {300} and {211} diffractions for particles synthesised using 120 minute against the carbon number in the alkyls chain of the solvent is presented in Figure 1e. It can be seen from Figure 1e that the full width at half maximum (FWHM) decreases monotonically with increase in carbon number in the alkyl chain confirming that as the carbon number in the alkyl chain increases, the particle size increases.

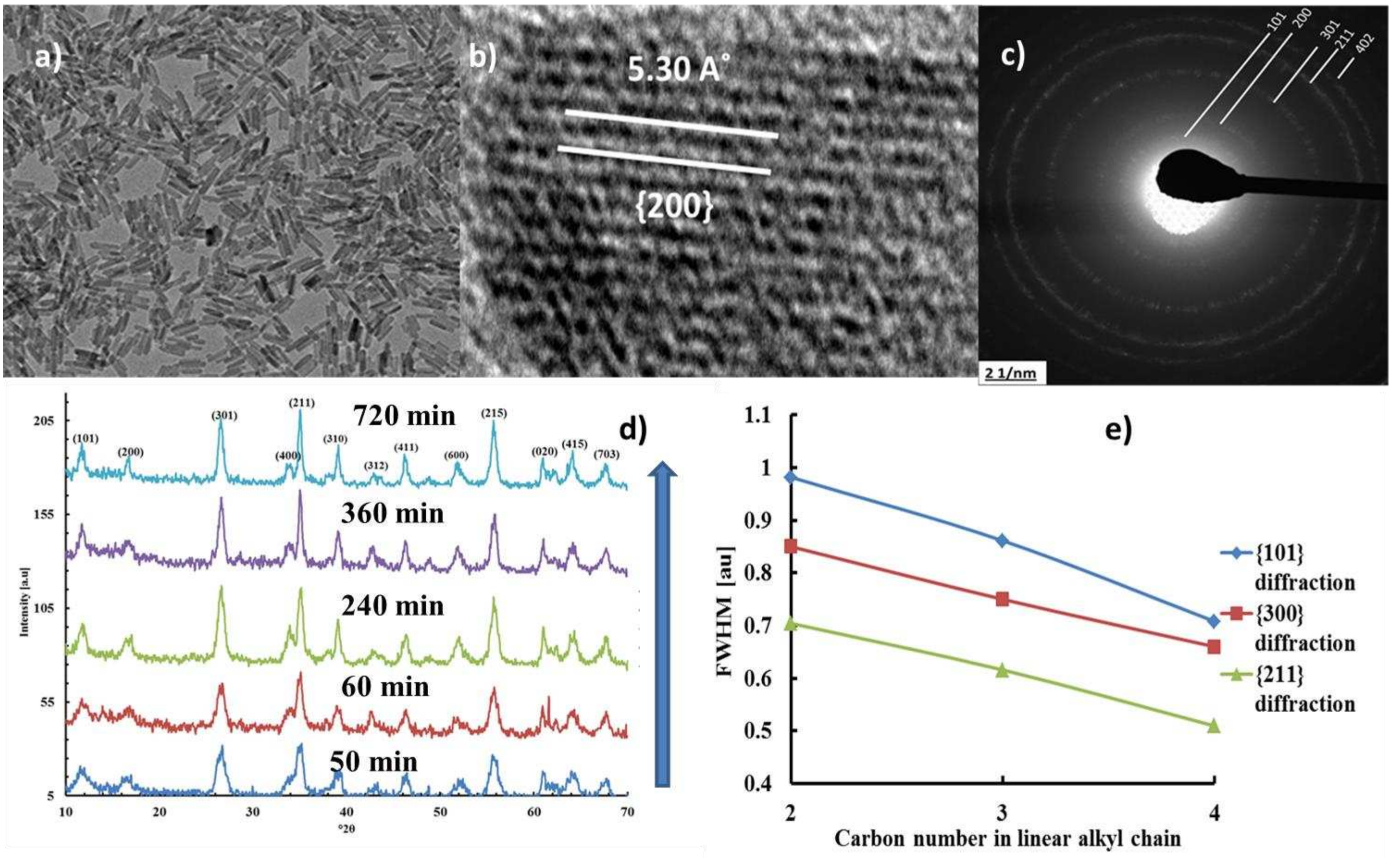


Figure 1. Reaction products obtained at 100℃ for all the different solvent used. In a) Monodispersed nanoparticles observed after 60 minutes of synthesis time, b) d spacing corresponding to the {200} plane of the akaganeite nanoparticles, c) SAED patterns of the β-FeOOH nanorods, d) typical XRD patterns obtained at different synthesis time and e) FWHM comparison of different peaks obtained for particles synthesized using different solvents.

3.2 Effect of alcohol on the growth mechanism of the β-FeOOH nanorods

3.2.1 Observation of OA mechanism via HRTEM

It was shown in Figure 1a that uniform akaganeite nanorods are formed after 60 minutes of synthesis time. As the synthesis time increases the particles tend to aggregate themselves when butanol or propanol was used as solvent. This can be observed from the TEM image in Figure 2a and 2b. It is suggested that once a particle pair is formed via O-A mechanism the radius of the new larger particles is smaller than twice the radius of the two primary particles [4]. Hence the distance between the new particles and other adjacent particles increases. Aggregation ensures small distances between the nanoparticles as can be seen form Figure 2a which provides the possibility of coarsening via oriented attachment. Twin rods and defects of nanorods are observed after a synthesis time of 360 minutes (Figure 2b). To understand the growth kinetics the microstructure and crystal morphology must be evaluated in detail. Figure 2c shows the growth of akaganeite nanorods. The big single crystal which is dotted with red lines in Figure 2c is composed of three small rods which are crystallographically oriented. This was observed after 360 minutes. So, it can be said the big single akaganeite nanorods (dotted red line in Figure 2C) were composed of three other akaganeite nanorods which are marked as A, B and C inside the red dotted line in Figure 2c. The arrowhead marks mark indentations, interpreted to be the interfaces between assembly units. The schematic outline in Figure 2d illustrates the observation in Figure 2c. A similar observation was also reported in the synthesis of ZnS nanocrystal [4]. The authors reported that a big single ZnS nanocrystal can also be formed by combination of two, three, four or five small ZnS nanocrystal. The growth process (Figure 2c) can also be described as defects such as twins or stacking faults which can be observed during the O-A growth process [3]. Once formed during the attachments it is possible to preserve the defects in the following growth process. So it can be said that two or more nanorods attach themselves together in specific orientation to form another nanorods. It can be seen from Figure 2b, c & d that the particles attach themselves together in a side by side orientation that increases the particle diameter. Once formed during the attachments it is possible to preserve the defects in the following growth process [19]. It can be seen from Figure 2b & c that the particles attach themselves together in a side by side orientation that increases the particle diameter. O-A mechanism is an effective approach in favour of synthesising nanorods or nanowires in one dimension [20]. An assumption was made in the literature that nanoparticles dispersed in a liquid medium exhibit a high degree of freedom for rotation and translation motion. Hence growth by means of oriented collision should be more effective than surface mechanisms in suspension [21]. The growth of the akaganeite nanorods in both longitudinal and transversal direction can be assumed as oriented collision of two nanorods asymmetrically. If two nanoparticles of two different length or same length attaches together not symmetrically (can also be seen from Figure 2b & c in the red dotted lines) due to high degree of freedom for rotation and translation, an increase in particle length and diameter will occur. Figure 3a schematically illustrates the growth of the nanorods in the longitudinal direction. However, if the growth of the nanorods in the longitudinal direction follows these assumed mechanism, a broader and not symmetrical particle length size distribution would occur. The reason behind this is that the nanorods attach together in side by side manner rather end to end manner and the attachment symmetry is random. This would eventually result in inconsistent particle size distribution in both longitudinal and transversal direction. It can be seen from the particle size distribution (Figure 3b and c,) that the distribution of particle sizes becomes inconsistent and asymmetrical over time. As the time increases, the shape of the distribution curve shifts from Gaussian distribution implying inconsistent distribution of the particle sizes. Thus it validates the assumption regarding the growth of the nanorods via O-A mechanism for the particles synthesised under the reported conditions. However signs of OA mechanism were not observed from the HRTEM images of the particles synthesised with ethanol and methanol as solvent. The particle size (diameter) distribution curves (Figure 3d) at different synthesis time represents approximate bell shaped curve and as the growth time progresses the distribution curves become more spread out. This hints towards a diffusion based growth i.e. OR kinetics. However kinetic evaluation is necessary. Synthesis conditions where OA mechanism dominates, should be avoided if production of uniform nanoparticles with specific sizes and well defined structure is desirable.

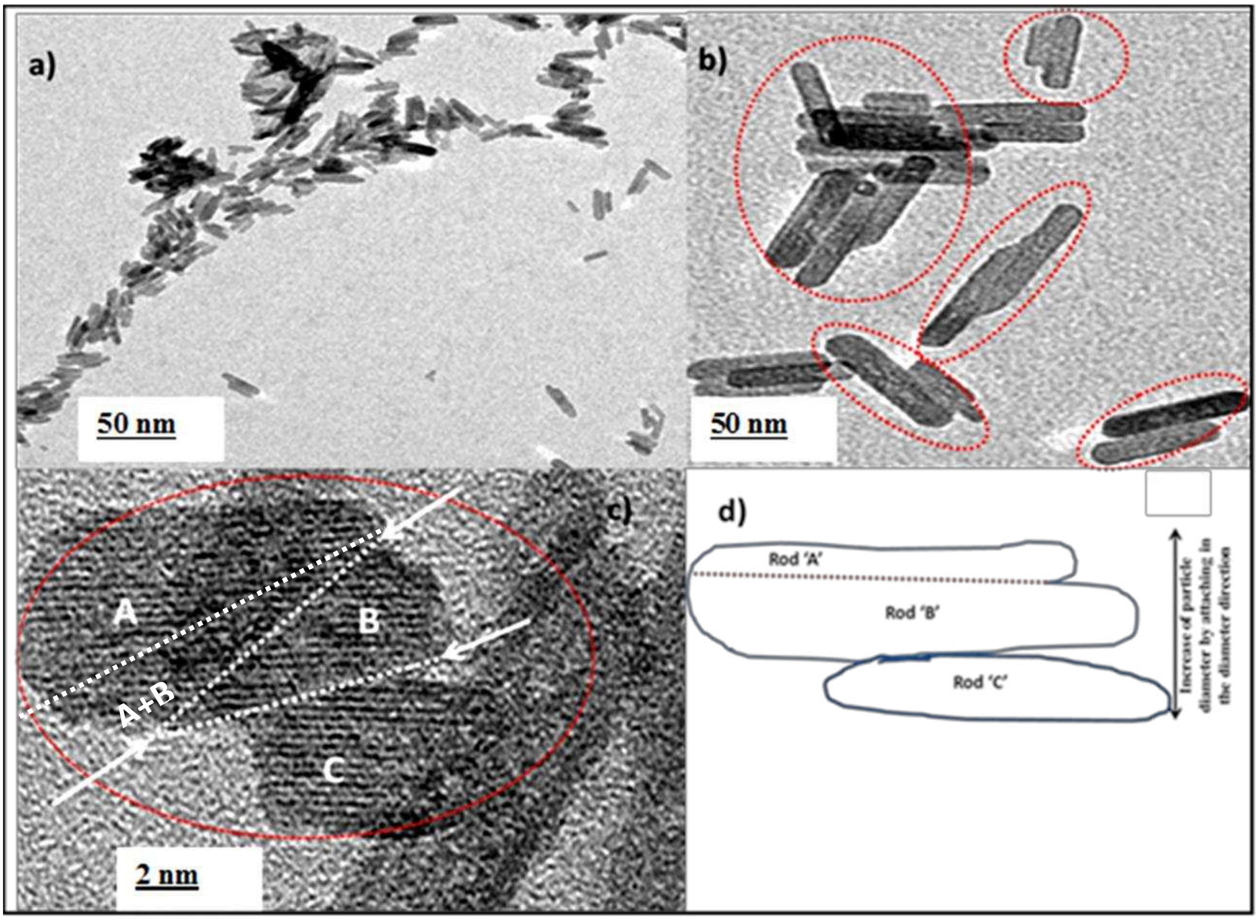


Figure 2: Aggregation of nanorods were observed with increasing synthesis time. In a) Nanorods starts to aggregate after 240 minute, b) Twins and stacking of particles are observed as the reaction time increases to 360 minutes, c) HRTEM image showing three coalesced akaganeite particles and d) Schematic illustration of coalesced akaganeite nanorods

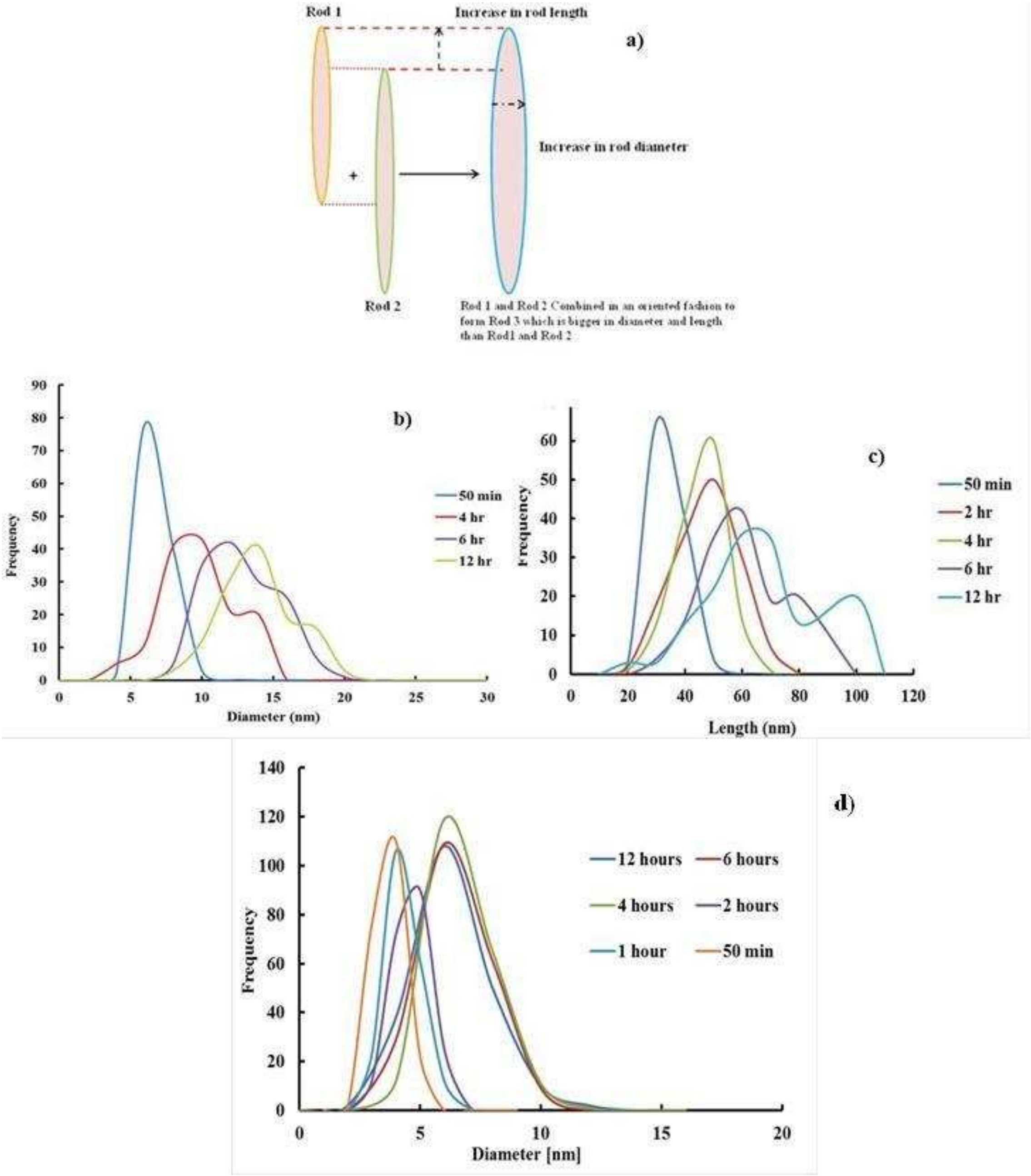
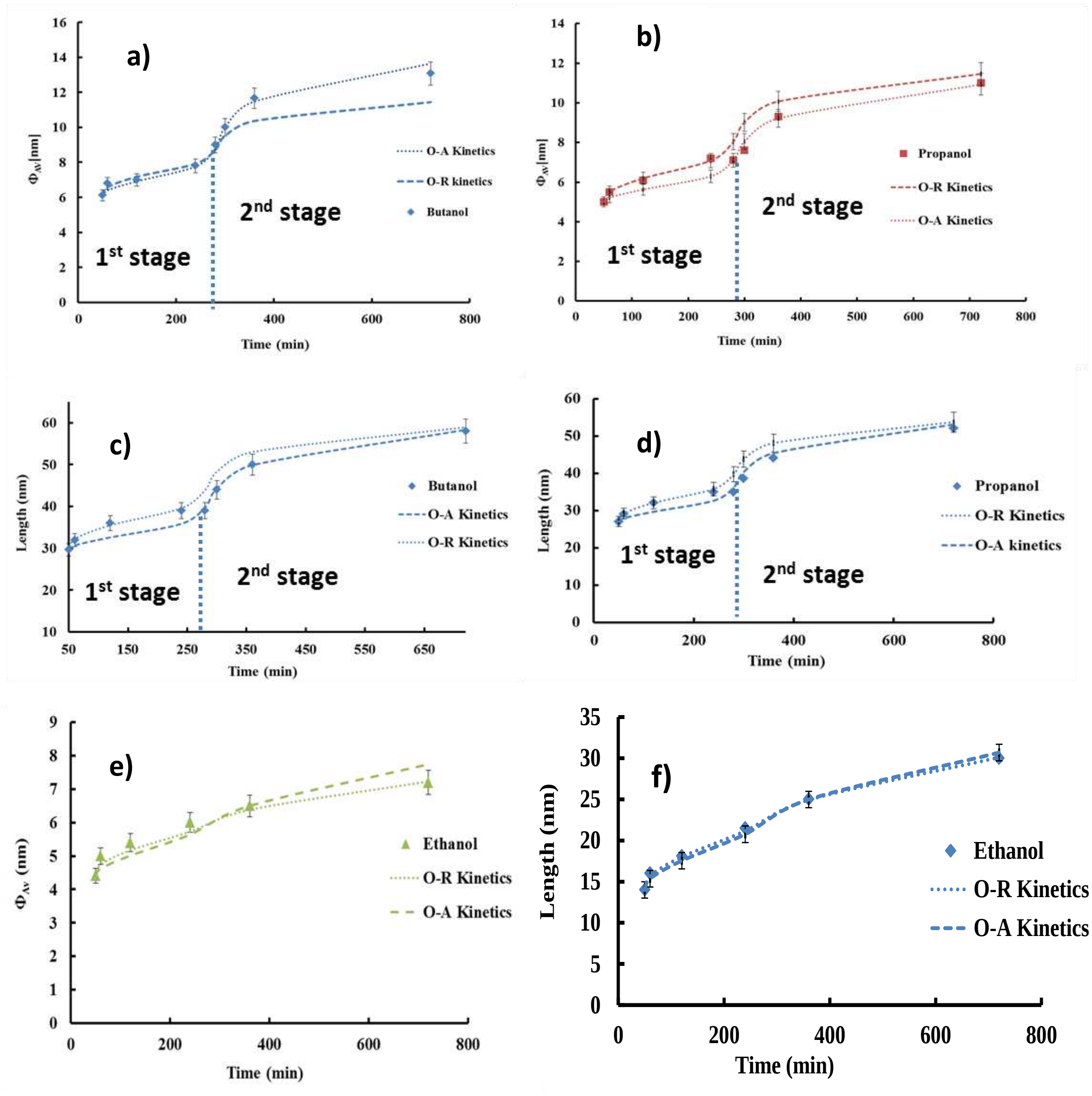


Figure 3: a) Schematic illustration of the growth of the nanorods via OA mechanism, b & c) Size distribution of the particles synthesised using butanol as solvent and d) Size (diameter) distribution of particles synthesised using ethanol as solvent

3.2.2 β-FeOOH growth kinetics in the presence of different alcohols

The average particle size versus time at 100℃ is presented in Figure 4 a-f. Figure 4a & b presents the diameter of the particles synthesized using butanol and propanol as solvents respectively. Figure 4c & d presents the length of the particles synthesized using butanol and propanol as solvents respectively. It can be seen from Figure 4a & b that the particle diameter increases in two stages. In the first stage the growth of particle diameter follows a power law. Classical OR kinetics can be used to describe the growth in first stage but the second growth stage does not follow the classical OR kinetic. The second growth stage is described by the OA kinetic. A similar trend is also observed in the growth of the particles towards the longitudinal direction. The similarity between the observations in both directions complement each other and shows that the growth of β-FeOOH is a two stage process in which the first step is dominated by the classical OR kinetics and the second growth stage is dominated by OA kinetics. This observation also validates the assumption (Figure 3a) towards the growth of the β-FeOOH nanorods in the length direction. The round shape and smooth edges of particles (obtained after 60 minute of synthesis time) observed in Figure 1a also confirms the growth of these particles via OR kinetics. Observation of irregular shape and abrupt edges in particles with increasing time also dictates growth via OA kinetic. Figure 4e & f presents the average particle diameter and length of the particles synthesized using ethanol as solvent at different time at 100℃. It can be seen from Figure 4e & f that the both kinetic model fits the experimental data however it is difficult to distinguish which mechanism is dominant over which between the two mechanisms. The R^2 value was found to be 0.98 and 0.9 for OR and OA mechanism (diameter direction) respectively when ethanol and methanol was used as solvent. On this basis it can be speculated that OR mechanism was dominant over OA mechanism. But the effect of each mechanism cannot be neglected due to the close presence of both mechanisms. The simultaneous occurrence of these two mechanisms is a common phenomenon and has been well noted [3]. Sometimes the simultaneous occurrence of both growth mechanisms is accompanied with phase transformation [3]. All of these lead to difficulties for investigating the size dependent crystal growth mechanism, especially kinetically [3]. The rate constants, k for both OR, (k_{OR}), and OA, (k_{OA}) kinetic and the exponent, n for OR kinetic was obtained using multivariable regression. A similar method is reported in the literature [22, 4]. The rate constants obtained for both kinetics are presented in Table 2.



[N.B. The error bars in Figure 4 a-f presents an standard error of 5% compared with the experimental data and the growth kinetics]

Figure 4: Experimental data and fitting of classical O-R and O-A kinetics. In, a) Growth of particles (synthesized using butanol as solvents) in the transversal direction, b) Growth of particles (synthesized using propanol as solvents) in the transversal direction, c) Particle growth (synthesized using butanol as solvent) in the longitudinal direction, d) Particle growth (synthesized using propanol as solvent) in the longitudinal direction, e) Particle growth (synthesized using ethanol as solvent) in the transversal direction & f) Particle growth (synthesized using ethanol as solvent) in the longitudinal direction

Table 2: Rate constants obtained for different growth mechanisms in both growth directions

	k_{OR} (min^{-1})	k_{OR} (min^{-1})	k_{OA} (min$^{-1/3}$)	k_{OA} (min$^{-1/3}$)
Solvent	Transversal	Longitudinal	Transversal	Longitudinal
Butanol	0.12	0.66	0.0036	0.0026
Propanol	0.10	0.47	0.0035	0.0024
Ethanol	0.07	0.27	0.0032	0.013
Methanol	0.08	0.30	0.0033	0.010

The exponent, n for O-R kinetic was found to be ~3 for both growth in transversal and longitudinal directions. A value of ~3 implies that the growth is controlled by the volume diffusion of ions in the matrix [4]. It can be seen from Table 2 that the OR rate constant, k_{OR}, is higher than the OA rate constant, k_{OA}, for both length and diameter. That implies the growth is slower in the second stage than the initial rate in the first stage. Also The rate constant k_{OR}, in longitudinal direction is much larger than the k_{OA} for transversal direction. This explains why the length of the particles changes rapidly than the diameter over time. Higher growth rate in the longitudinal direction than the transversal direction was also reported in the synthesis of silver nanorice [23] where the first growth stage is dominated by OR kinetics and then the latter is OA kinetic.

3.3 Relationship between alcohol surface tension and particle growth rate constants

Surface tension is of crucial importance in the formation of uniform nanorods [10,6]. However, no attempt was made in the literature to show a quantitative relationship between solvent surface tension and particle growth characteristics. In this study room temperature surface tension value of pure alcohols were directly related to the particle growth rate. It can be seen from Table 3 that the rate constants increases (for both mechanism in all directions) with the increasing surface tension of alcohols (For butanol, propanol and ethanol). The growth rate of the particles synthesised with methanol deviates from the aforementioned trend. It can be explained with the fact that methanol has very low boiling point (64˚C) compared to the other solvents used in this study. So it can be postulated that methanol as solvent in the solvo-thermal process can reach a critical state and then modify the physico – chemical properties of the reactant. This phenomenon can also be explained from the growth kinetics point of view. When butanol and propanol was used as solvent there were two distinct growth stages and the growth rates were evaluated separately due to the pure existence of only one mechanism in each stage or the effect of each mechanism on the others was negligible. When methanol and ethanol was used OR mechanism was dominant over OA mechanism but the effect of each mechanism cannot be neglected due to the close presence of each mechanism. The goodness of fit was found to be R^2 = 0.98 and 0.90 for OR and OA mechanism (transversal growth) respectively when ethanol was used as solvent. The R^2 value was found to be 0.99 and 0.98 for O-R and O-A mechanism (diameter direction) respectively when methanol was used as solvent. The very close existence of two mechanisms in the case of particles synthesised using methanol as solvent might have contributed somehow towards each other growth and hence a higher growth rate was found in the case of particles synthesised using methanol as solvent. Figure 5 presents the relationship between solvent surface tension and the rate constant, k_{OR} obtained for the growth of the nanorods in both transversal and longitudinal directions. An exponential relationship was used to describe the relationship between rate constants and the solvent surface tension (Figure 5a). One might try to raise issues on the applicability of the shown relationships based on the presence of few data points. But the validity of the relationships can be checked with an assumption that if the relationship is true then particles synthesised with different surface tension alcohol would possess also a similar trend. This will be due to the presence of exponential relationship between surface tension and rate constants under the reported conditions. To validate the hypothesis an independent test was conducted in the laboratory by another student using octanol as a solvent under identical reaction conditions. Figure 6 presents the natural logarithm of surface tension values of alcohol against the particle diameter and length obtained at 0.05M and 100˚C using a synthesis time of 2 hrs. It can be seen from Figure 6 that an exponential relationship exists between the alcohol surface tension and particle diameter and length thus also validating the initial hypothesis. The surface tension was evaluated against the k_{OR} kinetic only due to the fact that from the analysis it was found that k_{OR} is significantly higher than k_{OA} implying significant particle sizes have grown even before the OA kinetic dominates.

Table 3: Relationship between surface tension and the k_{OR} for both direction

		K_{OR} (min^{-1})	
Solvent	**σ (mnm^{-1}) (100% alcohol at 25˚C)**	**Transversal**	**Longitudinal**
Methanol	22.75	0.08	0.30
Ethanol	22.27	0.07	0.27
Propanol	23.7	0.10	0.47
Butanol	24.7	0.12	0.66

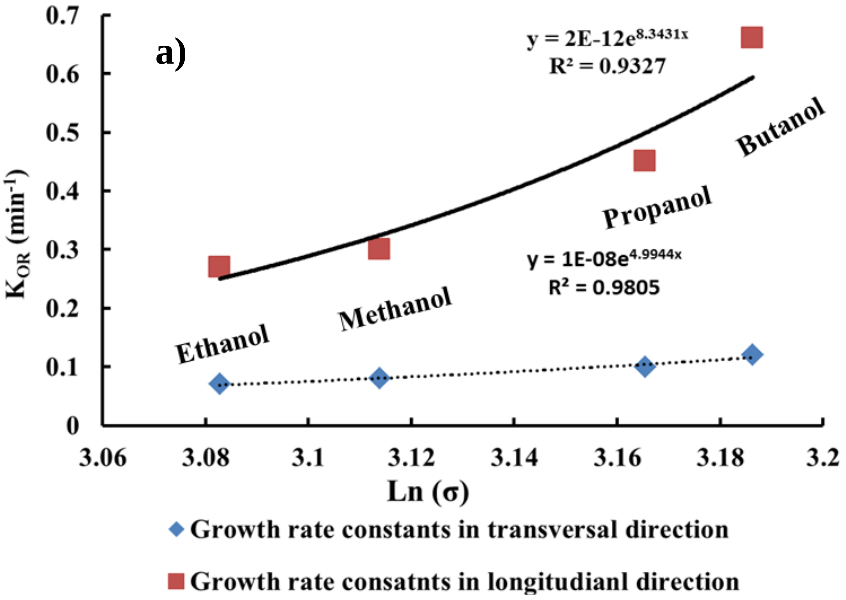


Figure 5: a) Relation between surface tension of pure alcohol at 25˚C and growth rate constants

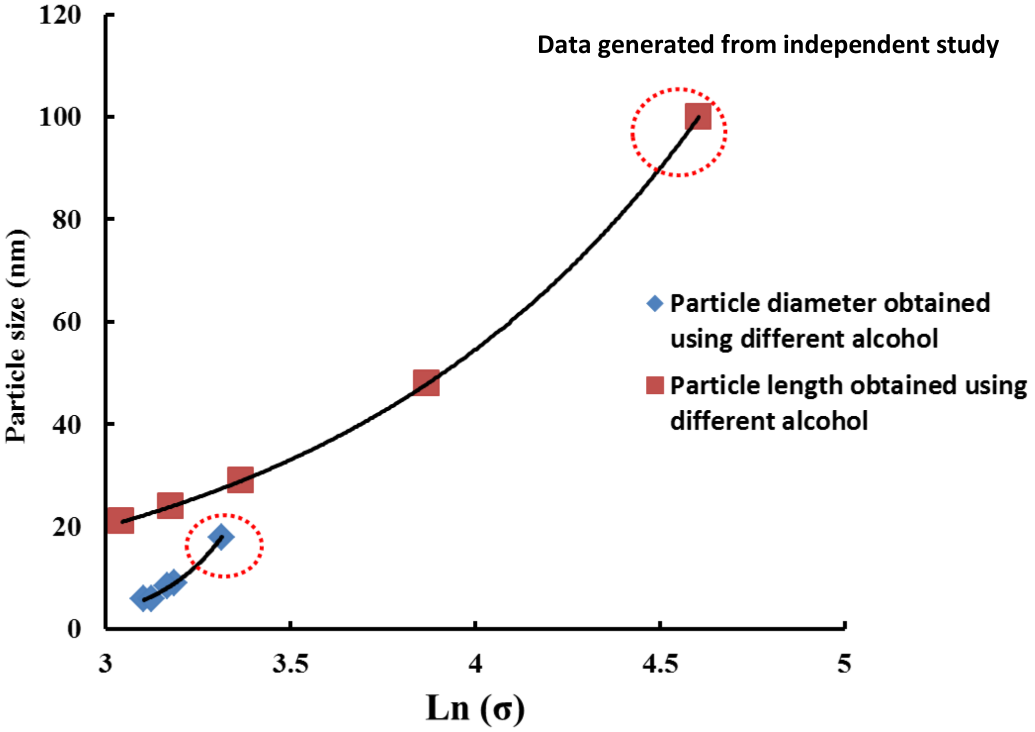


Figure 6: Illustration of the exponential relationship between alcohol surface tension and particle sizes

The electrostatic interaction between particles in solution was discussed by Penn from the OA growth point of view [24]. The interactions such as electrostatic force and van der Waals are assumed as the main ingredients determining the kinetic rate constant in OA growth. Riberio [26] described the growth behaviour of nanoparticles via OA growth as the diffusion and coagulation of colloids. It was concluded that the viscosity of the medium play an important role in the growth via OA mechanism. This viscosity relation is governed by an inverse proportional relationship with respect to the rate constant, k_{OA}. However, this aspect is not included in this study and will be reported later.

3.4 Development of generalized correlation to predict particle growth

In this study a two level three factor factorial design was used to identify the interactions between process parameters that have been used to synthesise the β-FeOOH nanorods. Preliminary studies have shown that the particle morphology is very sensitive to reaction temperatures and pH. Because of that, reaction temperature and pH was omitted from the factorial trial for simplicity sake. Only butanol was used as solvent to synthesise the particles. Table 4 presents the real amount of each parameters are used at low and high levels which is assigned by a positive (+) and negative (-) sign respectively.

Table 4: Real amount of each factor used in the factorial trial experiments

Factors	Low level (-)	High level (+)
A: $FeCl_3$ concentration [M]	0.05	0.5
B: % Butanol to water ratio	30	90
C: Time (h)	2	12

3.4.1 Evaluation of the effects of factors and the interaction between the factors on particle growth

The effects of three different parameters were evaluated using a two level factorial trial experimental design. This implies that 8 experiments were conducted to evaluate the interactions of each process variables. Table 5 presents the obtained aspect ratio at different experimental conditions. Particle aspect ratios were used as response for the two level factorial trials to keep consistency and simplicity in the analysis. The factorial design can cover the main and interaction effects of the parameters within the whole range of selected parameters. According to the sparsity-of effects principle in factorial design, it is most likely that main (single factor) effects and two-factor interactions are the most significant effects, and the higher order interactions are negligible [27].

Figure 7 presents the effect of the studied parameters and interaction effect between parameters on obtained aspect ratio of the particles. Evaluation of the effect of principal factors revealed that these parameters have positive effects on the obtained aspect ratios. % alcohol to water ratio and time shows the most significant effect to achieve maximum aspect ratio. According to positive effects of these variables, it can be noticed that an increase in solvent ratio and time increased the particle aspect ratios. The interaction between the solvent ratio and time also has the most significant effect in achieving maximum aspect ratio.

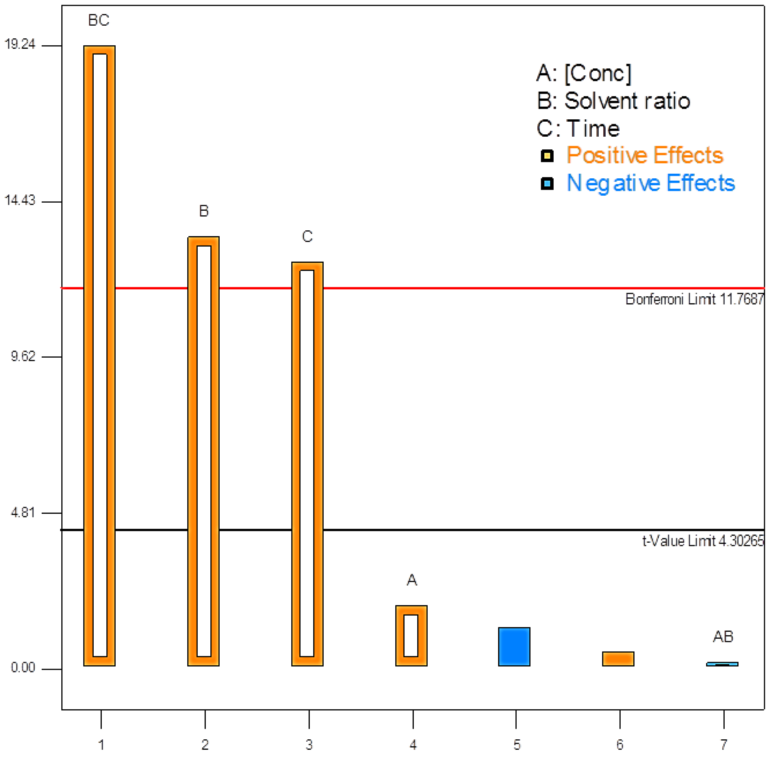


Figure 7: Estimated effects of factors on particle aspect ratio using factorial design

Table 5: Results obtained for a two level factorial design

Samples	$FeCl_3$ concentration [M]	% alcohol to water ratio used as solvent	Time (h)	Obtained aspect ratio
1	0.05	30	12	6
2	0.50	30	12	7
3	0.05	30	2	8
4	0.05	90	12	13
5	0.50	90	12	13
6	0.50	30	2	8
7	0.05	90	2	6
8	0.50	90	2	7

Based on the significance of effects of the parameters on the particle aspect ratio and the established relationship between solvent surface tension and particle growth (section 3.3) a generalized correlation is proposed:

$$Y = \beta_o \sigma + \sum_{i=A} \beta_i X_i + \sum_{i=A} \sum_{j=A \neq i} \beta_{ij} XiXj + \varepsilon$$ Equation 3

Where, Y, is the predicted response (Aspect ratio in this case), X_i are the un-coded or coded values of the factors (concentration denoted by A, % alcohol to water ratio is denoted by B and time is denoted by C), β_o is a constant, σ is the surface tension of alcohol used, β_i are the main effect coefficients for each variable and $\beta_{i\,j}$ are the interaction effect coefficients. The corresponding response model for the obtained aspect ratio of the particles which are valid for un-coded factor is:

$$Y = 0.25\sigma + [A] - 0.29[B] - 0.50[C] + 0.07[AB] + 0.009[BC]$$ Equation 4

Statistical analysis was performed in design-expert® software and it was found that Equation-4 has an F-Test / Model F-value of 141.91. This implies that the model is statistically significant and there is a 0.70% chance that a Model F-value that high is due to data noise. The P-value of the model was found to be less than 0.05 indicating model terms are significant. The term B, C and BC in Equation 4 is statistically mostly significant model terms. Figure 8 presents the comparison between predicted and actual aspect ratio obtained. The average percentage uncertainty between the predicted and the actual aspect ratio was found to be between ±2%.

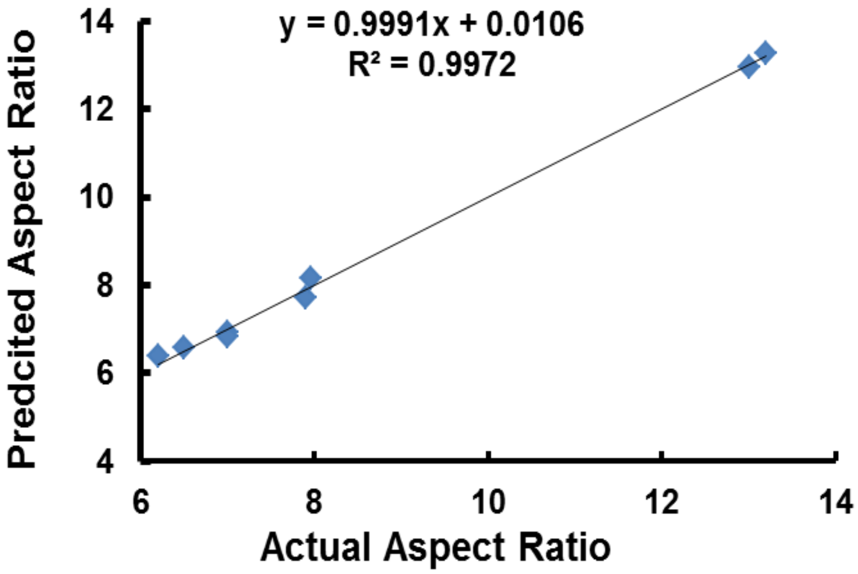


Figure 8: Comparison between actual (data obtained from factorial trial) and predicted aspect ratio.

Independent experiments at random sequence were conducted to further validate the model. Propanol, butanol and ethanol were used as a solvent to further illustrate the relationships between solvent surface tension and particle growth. Figure 9 presents a comparison between experimental and model data. It can be seen from Figure 9 that the model predicts the particle aspect ratio very well, and the uncertainty range is within ±25% in all cases. Considering the nanoscale of the materials this model should be considered reliable under the reported conditions.

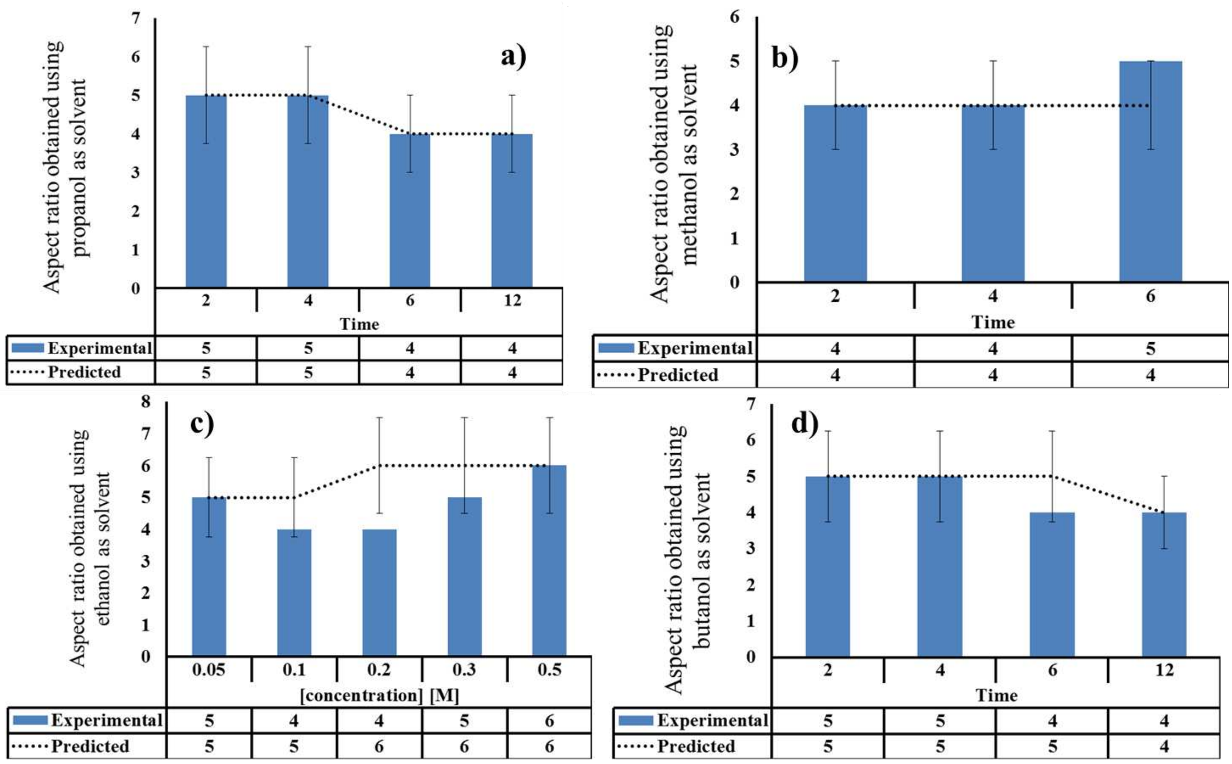


Figure 9: Comparison between experimental and predictive data

4. Conclusion:

The hydrothermal growth of akaganeite nanorods can be controlled by selectively choosing a solvent. Growth regimes of particles synthesised with butanol and propanol solvents can be divided in two distinct stages. The first stage of the growth for particles synthesized with butanol and propanol was described by classical OR kinetics and the second stage of growth were described by the newly developed OA kinetics. The two-stage growth process can be attributed to the presence of the butanol and propanol solvents only. Simultaneous occurrences of the two mechanisms were observed in the growth of the particles synthesized with ethanol as solvent. A quantitative relationship between growth rate constants and alcohol solvent surface tension was established and later validated. Statiscally designed experiments were conducted to identify the interactions between process parameters. A generalized correlation was developed by correlating the surface tension of solvents with different process parameters to predict β-FeOOH aspect ratios for the first time. This correlation predicts particle aspect ratios with acceptable confidence. This work is a stepping stone in understanding the relationship between particle growth and solvent surface tension but provides the basis for more work to have a better theoretical understanding.

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