

One-step synthesis of flower-like η - Al_2O_3 via supercritical hydrothermal method

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In this Letter, flower-like η - Al_2O_3 nanostructure was synthesised via hydrothermal method without any surfactant or further calcination. A molten salt bath rose the reactor temperature as much as 500°C to achieve the supercritical condition. Such a high temperature caused a rapid one-step synthesis in two minutes. $\text{Al}(\text{NO}_3)_3$ and NaOH were the only precursors. Synthesised powders were investigated by X-ray powder diffraction and scanning electron microscope, and the specific surface area was also determined by N_2 adsorption–desorption analysis. Increasing reaction time >2 min caused undesired Ostwald ripening. So instead of giving more time, a small amount of NaOH was added to form the η - Al_2O_3 phase. Moreover, the morphology of η - Al_2O_3 changed to flower-like by increasing the density of the supercritical fluid. Finally, the probable mechanism of flower-like morphology formation was proposed in two steps.

1. Introduction: Alumina exists in several polymorphs, including α , γ , δ/θ and η [1, 2]. This polymorphism can be useful in various applications such as water treatment, gas adsorption, catalysts etc. [3–14].

It has been found that alumina phases transform to each other over the temperature changes [15, 16]. These transformations happen in a sequence of γ/α - $\text{Al}(\text{OH})_3$ to ρ - Al_2O_3 and ρ - Al_2O_3 to η/γ - Al_2O_3 and finally all of these metastable phases irreversibly transform to the stable α - Al_2O_3 at around 1050°C [17].

Except α - Al_2O_3 , the other metastable phases can be used as catalyst support [18–30]. Between various phases of alumina, γ and η - Al_2O_3 , with similar structures, have been widely employed as catalysts or catalyst support in the Fischer–Tropsch process, hydrocracking and so on [31–33]. Compared with γ - Al_2O_3 , η - Al_2O_3 has higher activity due to its lower surface energy and higher specific surface area, which is proper for catalytic applications [34, 35].

Owing to its lower surface energy, η - Al_2O_3 becomes more stable by the reduction of particle size rather than the other polymorphs. Moreover, it is stable over the temperature range at which most of the catalytic reactions take place.

To achieve the maximum reachable active surface, we have to produce anisotropic nanostructures by manipulating the morphology of the synthesised phases. In this regard, mass production of η - Al_2O_3 nanostructures with needed size and morphology is highly requested, since each morphology exhibit properties which are desired for a particular application. Between the well-known morphologies (i.e. spherical, cubic, rod, wire, tube, plate-like, flake, film, polyhedral and so on), hierarchical flower-like structures present an outstanding active surface area which is proper for catalysts.

Despite having these advantages, not much attention has been paid to the η - Al_2O_3 synthesis. Pradhan *et al.* [36] synthesised η - Al_2O_3 via a wet chemical route. They produced η - Al_2O_3 by calcination of basic aluminium sulfate at 900°C. In another research, η - Al_2O_3 was produced by calcination bayerite (γ - $\text{Al}(\text{OH})_3$), which had been formed from the hydrolysis of NaAlO_2 solution [34]. Seo *et al.* prepared η - Al_2O_3 using a two-step approach, i.e. sol–gel preparation by aluminium-tri-sec-butoxide, then calcination at 300–700°C [37]. Osman *et al.* [25, 26, 38] reported η - Al_2O_3 synthesis via precipitation of $\text{Al}(\text{NO}_3)_3$ and AlCl_3 solutions by ammonia followed by calcination and obtained precipitates at 300–550°C.

In all previous researches, η - Al_2O_3 has been synthesised by a two-step approach, including AlOOH synthesis and calcination. As this calcination is carried out in a temperature range of 400–700°C, and because of the long time that it takes, synthesis procedures usually take too much time and energy, which makes them unprofitable for industrial scale-up.

Herein, for the first time, a rapid one-step high temperature supercritical hydrothermal synthesis of Al_2O_3 without calcination has been reported. In this work, flower-like η - Al_2O_3 nanostructure was produced in 2 min by tuning the synthesis parameters such as time, NaOH and supercritical solution density at 500°C.

2. Materials and methods

2.1. Reactor: A double-layered reactor chamber (Fig. 1a) was designed and manufactured with a capacity of 24 ml. The outer layer was made of hardened hot work steel (AISI H13), which is a heat and thermal shock resistant steel, and the inner layer was made of corrosion-resistant stainless steel AISI 316L. The reactor's opening cap was sealed with a carbon heat resistant sealant. This set up with a safety factor of 4 was prepared to endure 600°C temperature and 60 MPa pressure. In order to prohibit heterogeneous nucleation and growth, the surface of the inner layer was polished to reach a mirror-like surface (Fig. 1b).

2.2. Synthesis procedure: The adequate amounts of $\text{Al}(\text{NO}_3)_3$ and NaOH (both were obtained from Merck, Germany) were dissolved in deionised water. Then, a specific volume of solution was charged into the carbon sealed reactor. The reactor was subsequently entered into the molten inert salt bath to be heated at desired temperatures, according to Table 1. After spending favourable time, the reactor was immediately quenched in cold water in order to prevent the reaction from advancing and to achieve the appropriate product.

Various experiments were carried out in this research for investigating different parameters' effects on the shape, particle size and synthesised phases. These factors included reaction time, NaOH concentrations and precursor solution volume, which are shown in Table 1.

2.3. Characterisation: Morphological investigations were carried out by the scanning electron microscope (SEM, XL30, Philips, Netherlands) and (SEM, AIS2100, Seron Technology, South Korea). The phases of synthesised powders were identified by

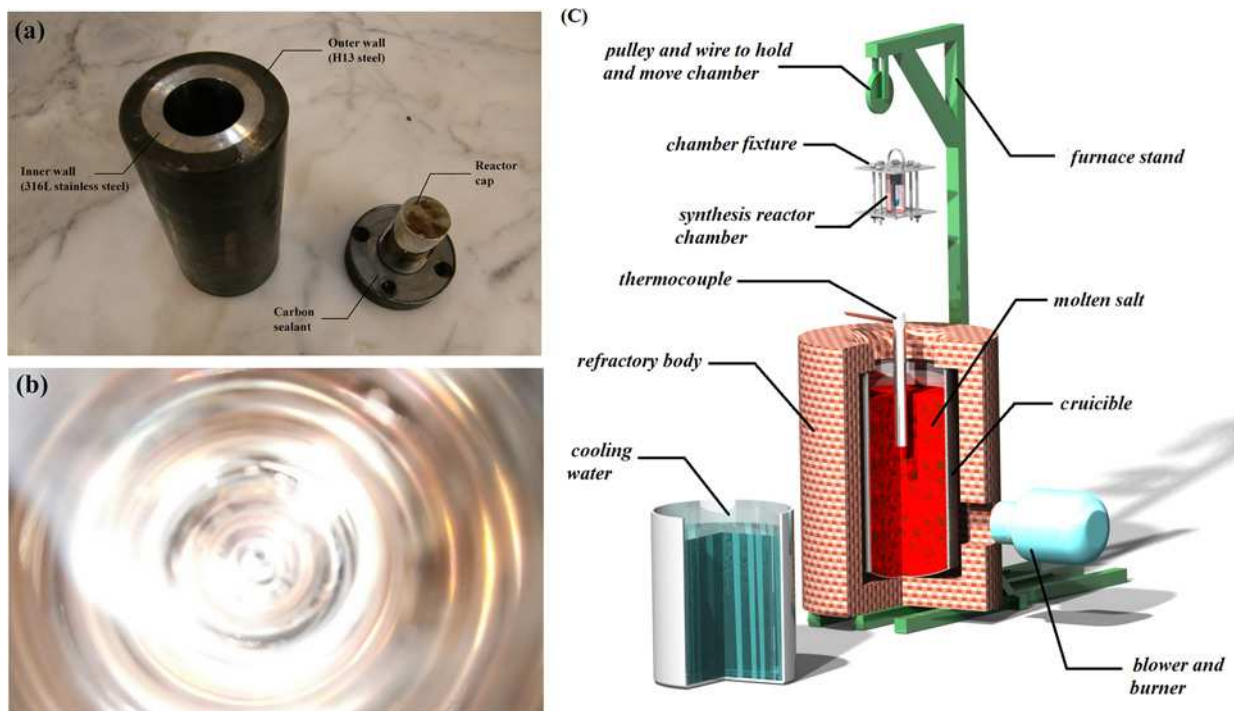


Fig. 1 Synthesis setup
 a Synthesis reactor
 b Mirror-like inner surface of the reactor
 c Schematic representation of the furnace, molten salt and quench water bath

Table 1 Nomenclature of samples and their synthesis conditions

Sample code	Time, min	[NaOH], mol/l	Density*, g/cm ³	Alumina, %
1	2	0	0.17	0
2	3	0	0.17	0
3	4	0	0.17	0
4	15	0	0.17	14
5	2	0.3	0.17	23
6	2	0.6	0.17	53
7	2	0.6	0.25	71
8	2	0.6	0.34	84

*Supercritical fluid density.

X-ray diffraction (XRD, Equinox 3000, INEL company, France) with Cu K α ($\lambda=0.15418$ nm) radiation. The pH of precursor solutions was measured by a pH meter (pH50+DHS, X.S. instruments, Italy). The specific surface area of the obtained η -Al₂O₃ powder was determined using adsorption and desorption of Nitrogen (BET, 3P micro 200, 3P Instruments, Germany).

3. Results and discussion

3.1. Appropriate time: Huge reaction rate makes the supercritical hydrothermal synthesis 1000 times faster than conventional hydrothermal one [39]. Owing to the high pressure and temperature, the supercritical hydrothermal condition has become an advantageous approach to the synthesis of high crystalline metal oxide compounds [40–42]. Time dependency of the particle morphology and phase were evaluated at various times. Fig. 2 shows the SEM micrograph of particles obtained from different reaction times (2, 3, 4 and 15 min). With an increase in reaction time, Ostwald ripening can be observed as a result of the time-dependent diffusive nature of this phenomenon. As this Figure shows, big particles cannibalised small ones, so that particle size distribution became

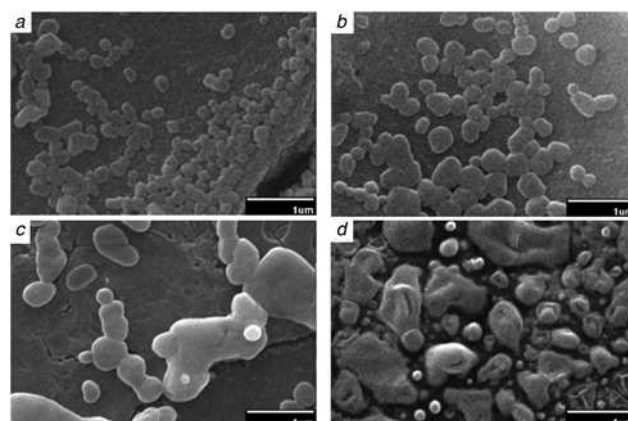


Fig. 2 SEM images of samples which show the reaction time effect on particle growth

a Sample 1 synthesised in 2 min
 b Sample 2 synthesised in 3 min
 c Sample 3 synthesised in 4 min
 d Sample 4 synthesised in 15 min

non-uniform. In 2 min, reaction time (Fig. 2a), there was not sufficient time for mass transfer, and particle sizes have not been influenced by Ostwald ripening.

Noguchi *et al.* [43] explained the supercritical hydrothermal reaction mechanism of Al₂O₃ in three different steps as follows:

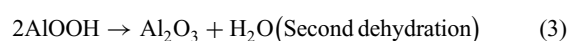
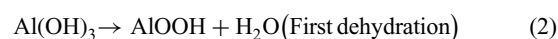
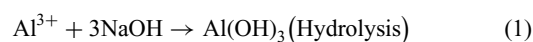


Fig. 3a shows the XRD pattern of sample 1 at 500°C and 2 min of reaction time without the presence of NaOH. The pattern indicates

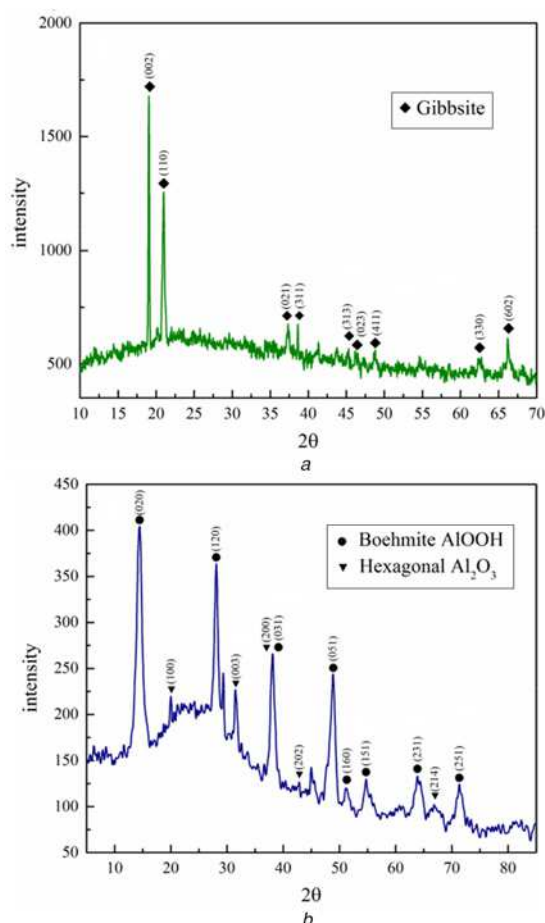


Fig. 3 XRD patterns of samples at different synthesis condition
a Sample 1 synthesised in 2 min
b Sample 4 synthesised in 15 min

that in this condition, only the hydrolysis reaction (1) occurred, and Gibbsite ($\text{Al}(\text{OH})_3$) was the only product. A comparison between samples 1 and 4 (Figs. 3*a* and *b*) gives us a clue that raising the reaction time from 2 to 15 min at 500°C causes the first dehydration reaction (2) to be completed by producing Boehmite.

To reach a desirable phase and morphology, proper time and temperature should be considered for the synthesis. Conventional hydrothermal synthesis carries out in a wide range of temperatures from 100°C up to the critical temperature of water (374°C). Also, in supercritical synthesis, the temperature is set to near the critical temperature (e.g. 400°C). In the continuous supercritical synthesis method, the reaction occurs at a fraction of a second while in supercritical batch, the reaction takes 10 min to a couple of hours to proceed at the range of critical temperature. For achieving the $\eta\text{-Al}_2\text{O}_3$ phase, the experiments were carried out at 500°C in this research. Owing to the increase in high temperature, nucleation and growth rates the precipitate formation is accelerated [44]. As it was discussed before, the increased time caused particles' secondary growth at high temperature. To eliminate undesired Ostwald ripening, a molten salt bath was used as a rapid heating source to speed up the reaction and finish it before secondary growth. Therefore, the experiments were performed in 2 min to prohibit Ostwald ripening. However, this time is not sufficient for boehmite or Al_2O_3 formation at 500°C . Thus, another remedy should be investigated to achieve these phases.

3.2. Synthesis $\eta\text{-Al}_2\text{O}_3$: Mineraliser is an important factor in inorganic hydrothermal synthesis. Hydroxides, halides, sulfides, carbonates etc. can be used as a mineraliser. Hydroxide is one of

the most effective anions in oxides synthesis in the precursor solution [45]. The solubility of the amphoteric species (such as aluminium oxide) is related to the mineraliser concentration [46]. Thus, in this research, the concentration of soluble Al-compounds was raised by adding NaOH. Besides, adding more OH^- – as one of the reactants in Al_2O_3 formation – causes the system to form more of it.

According to the XRD pattern of sample 6 ($\text{pH}=11$), which is shown in Fig. 4, increasing in precursor solution pH resulted in Diaspore (AlOOH) and $\eta\text{-Al}_2\text{O}_3$ formation.

The effect of NaOH concentration on the morphology of the particles is illustrated in Fig. 5. In these samples, NaOH increases from left to right. By increasing NaOH concentration, spherical particles transformed to plate ones. Further increase in NaOH concentration causes monomer concentration rise, which resulted in flake-like particles formation.

3.3. Synthesis of flower-like $\eta\text{-Al}_2\text{O}_3$: Another important factor in the supercritical state that affects morphology, is the supercritical fluid density. So, without making any changes in concentration, time or temperature, this factor was investigated for further morphological clarifications. As a consequence of liquid expansion, the final supercritical fluid volume is equal to the reactor volume.

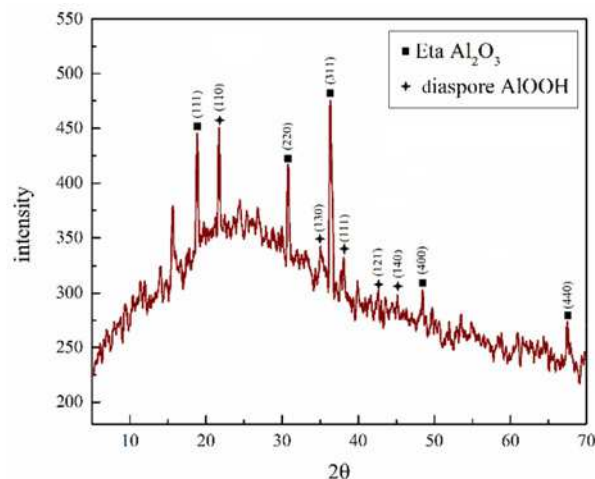


Fig. 4 XRD patterns of sample 6: 500°C , 2 min, $[\text{NaOH}] = 0.6 \text{ M}$, supercritical fluid density = 0.17 g/cm^3 (JCPDS file numbers of $\eta\text{-Al}_2\text{O}_3$ and diaspore are 00-047-1292 and 00-081-0465, respectively)

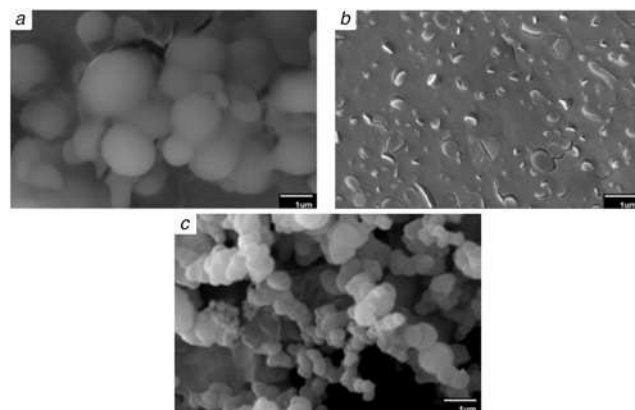


Fig. 5 SEM micrographs of
a Sample 1- $[\text{NaOH}]=0$
b Sample 5- $[\text{NaOH}]=0.3$
c Sample 6- $[\text{NaOH}]=0.6$

Since the reactor volume is constant, increasing the precursor solution volume raises the supercritical fluid density (4)

$$\text{Supercritical fluid density} = \frac{\text{Precursor mass}}{\text{Reactor volume}} \quad (4)$$

According to Figs. 6a–c, the supercritical fluid density increased from 0.17 to 0.25 and 0.34 g/cm³, respectively which led to a morphology trend from circular nanoflake to agglomerated particle and finally to the flower-like hierarchical structure at 0.34 g/cm³. Increasing the density from 0.17 to 0.34 g/cm³ caused Diaspore amount to decrease and η -Al₂O₃ became the predominant produced phase (Fig. 7).

The surface area of the product was also determined by N₂ adsorption–desorption analysis. The result in Fig. 8 shows that the Al₂O₃ affords a high surface area of 106.7 m²/g.

The yield of reactions measured by the weight loss in calcination at 900°C, and data was added to Table 1. Increasing time, NaOH concentration and supercritical fluid density caused dehydration reactions (2) and (3) advancement.

3.4. Suggested mechanism for flower-like η -alumina: As a result of doubling the solution density from 0.17 (sample 6) to 0.34 g/cm³ (sample 8), monomer concentration doubled, and the supersaturation increased significantly. In this condition, it was observed that a huge number of plates emerged rapidly from a single spot and formed particles with a hierarchical structure. If the driving force rises so much, due to the radial growth from the centre, hierarchical

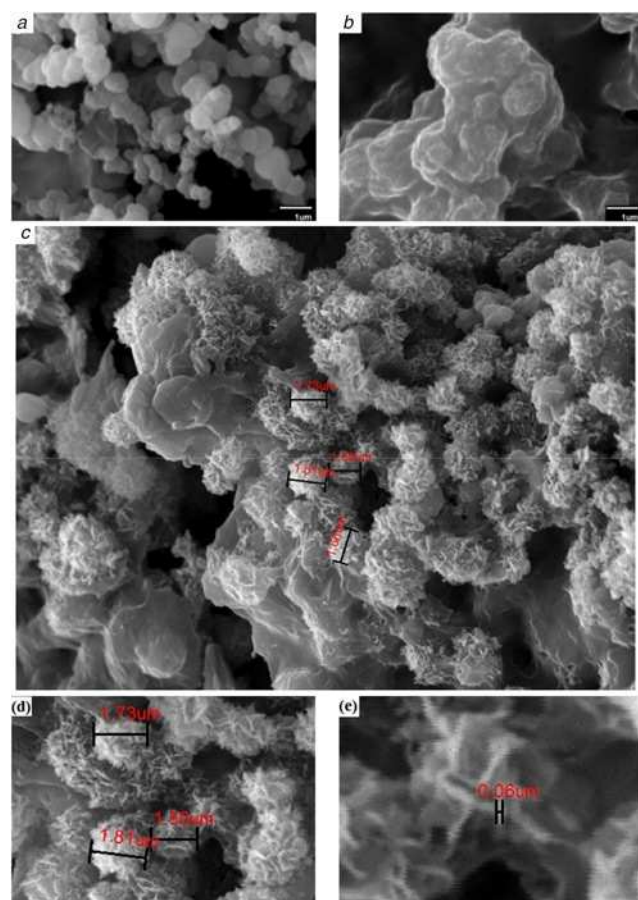


Fig. 6 SEM micrographs of
a Sample 6 with 0.17 g/cm³ supercritical fluid density
b Sample 7 with 0.25 g/cm³ supercritical fluid density
c–e Sample 8 with 0.34 g/cm³ supercritical fluid density in different magnifications

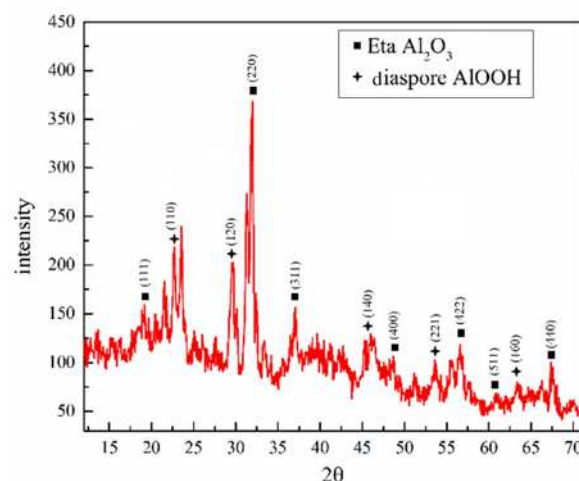


Fig. 7 XRD patterns of sample 8: 2 min, [NaOH] = 0.6 M, supercritical fluid density = 0.34 g/cm³

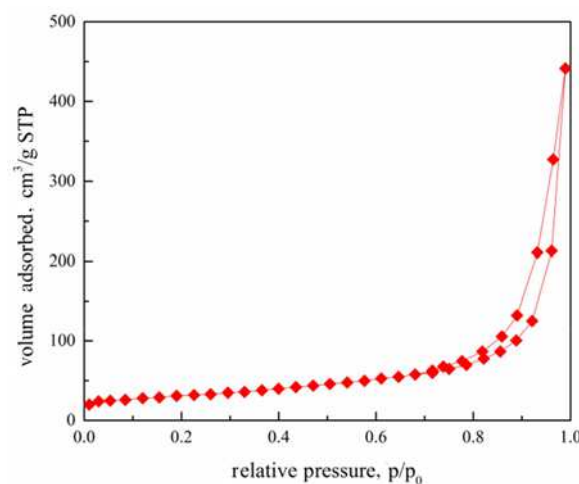


Fig. 8 N₂ adsorption/desorption isotherms of flower-like η -alumina

polycrystalline can be produced [47]. Herein, due to the huge increment in supersaturation, plates emerged from cores as a result of radial growth (Fig. 6c).

At the density of 0.17 g/cm³, η -alumina nanoflakes were formed from diasporic (Fig. 6a). The formation of nanoflake morphology in this situation is triggered by the naturally layered crystal structure of diasporic as the primary source of η -alumina. By raising the density, nucleation happened with high intensity. Owing to intense nucleation, a high number of spherical nuclei created and attached together to form nanosphere aggregates (Fig. 6b). The flower-like particle formation process included two steps. First because of high supersaturation, a high number of initial particles aggregate together to form spherical cores. Second, nanoflakes formed on the surface of these spherical cores (Fig. 6c). This lamellar growth of flower petals is similar to the nanoflake formation at low densities in the present work.

4. Conclusion: Eta alumina (η -Al₂O₃) powders were rapidly synthesised via a one-step supercritical hydrothermal route at 500°C without calcination for the first time. The synthesis time was reduced to 2 min by taking advantage of the molten salt bath as a rapid heating source. The influential factors of η -Al₂O₃ synthesis, such as reaction time, the dosage of NaOH and supercritical solution density were determined, and then a mechanism for the

production of flower-like morphology was suggested. It was found that adding NaOH boosts dehydration and oxidation reactions in the synthesis process; so that η -Al₂O₃ was produced effortlessly at basic pH. At a low density of the supercritical fluid, nanoplates of η -Al₂O₃ were produced. While by increasing the density, flower-like hierarchical morphology was formed. The flower-like particle precipitation mechanism consists of two steps. The first step is aggregating initial particles to form spherical cores, and then emerging two-dimensional nanopetals on the surface of these cores.

5 References

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