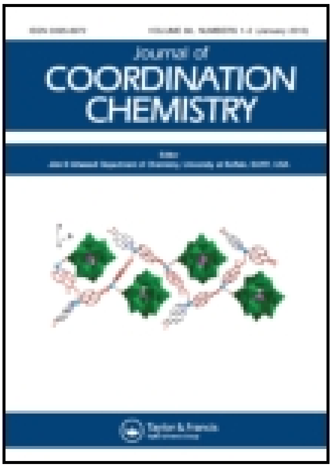

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Flower-like boehmite nanostructure formation in two-steps

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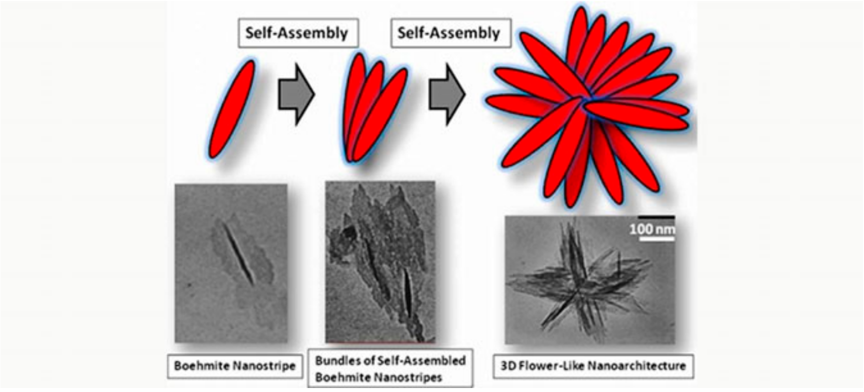

Reaction between $AlCl_3$ and TEA (triethanolamine) gave $Al(OH)_3$ colloidal nanocrystals that were precursors to nucleation and growth of boehmite under hydrothermal conditions. Transition electron microscopic (TEM) observations revealed that flower-like nanostructures were produced through a binary self-assembly system. In the first stage, nanostrips organize themselves to form a bundle, because of NH_4^+ and TEA. In the second stage, the bundles form flower-like nanostructures due to the interaction of nitrate with TEA. The size of the nanopetals (length 100–200 nm; width 100–150 nm; and thickness 20–70 nm) was measured through TEM. X-ray diffraction and Brunauer–Emmett–Teller (BET-N_2) results demonstrate that the obtained nanostructures were composed of a pure AlOOH phase with a surface area of $160\,m^2\,g^{-1}$. The effect of Cl^- on the growth of boehmite 3-D nanoarchitectures in the presence of NO_3^- was also investigated.

Keywords: Nanostructures; Hydrothermal; Self-assembly

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1. Introduction

Nanoscience has drawn much attention because of unique physical–chemical properties, i.e. high-elastic modulus, electronics, optics, lasing, sensing, magnetism, energy storage, biomedical sensors and electro-chemistry, and thermal and chemical stability [1–6]. Due to applications in industry, nanostructures based on metal oxide and hydroxides have been studied [7, 8].

Boehmite is one of the most important hydroxides because it is utilized for the preparation of different kinds of catalysts, coating e.g. aluminum foil, adsorbent materials, and optical materials [9, 10]. Also, boehmite is used for making a template in the preparation of core/shell materials [11]. Boehmite is also the precursor for preparing high-purity and high-strength monolithic α-Al_2O_3 ceramic [12]. Therefore, the morphology and production routes for nanoboehmite are important.

Mechanical properties of nanostructures should be superior to microstructures. Indeed, materials with the same composition can reveal different mechanical properties due to various morphologies [7, 13]. Among the extensive literature on the formation of 1-D nanostructures, boehmite nanostructure phases have been reported as nanoribbons [14], nanotubes [15], nanostrips [16], nanoparticles [17], nanowires [18], nanofibers [19], nanorods, and nanoflacks [20]. Characteristics of boehmite, such as its specific surface area and porosity, are clearly affected by the morphology of the boehmite precursor [21, 22]. Therefore, there are a large number of potential applications that might be realized by making new morphologies. For instance, control of nanoparticle size and shape affects their properties and application in nanodevices. Consequently, phase structure and morphology play roles in the properties of materials. Extra elements in the precursor solution can affect the morphology of the crystals during the growth from solution. Zanganeh *et al.* [23] prepared boehmite nanopetals (3-D) through self-assembly with TEA and Cl^- affecting morphology and growth of nanopetals.

Applications of inorganic nanostructures require synthesis of nanoparticles and arrangement of nanoparticles into 2-D or 3-D ordered super-lattices. Numerous elegant nanoarchitectures have been prepared by different techniques based on different mechanisms. For example, nanocomb [22, 24], nanofork [25], etc. with 2-D nanostructures, nanotube [26], hollow nanosphere [27], and tetrapods [28] have been prepared.

Different methods for synthesis of boehmite nanopowder have been reported, such as hydrothermal treatment [29], sol–gel [30], and spray pyrolysis [31]. The hydrothermal route has been reported to be an interesting and effective procedure because of the low temperature employed during the process and easy control of the morphology due to the synthetic conditions [32]. Therefore, hydrothermal processes have emerged as powerful routes for the fabrication of interesting nanostructures, particularly anisotropic nanomaterials [33, 34].

The aim of the present work is to acquire boehmite nanostructures by a self-assembly system of nanosized strips using a hydrothermal method.

2. Experimental details

The procedure employed for preparing AlO(OH) with 3-D nanoarchitectures is as follows: First, 10% vol. triethanolamine [$N(C_2H_4OH)_3$, TEA, Merck, Germany] was dissolved in 100 mL de-ionized water under magnetic stirring until pH of 10.5 for the reaction mixture was attained. Subsequently, $AlCl_3$ (analytical grade, Merck, Germany) powder was added to the solution during stirring to reach pH of 9. After that, CH_3COONH_4 (ammonium acetate, analytical grade, Merck, Germany) powder was added to the solution with stirring to reach pH of 8.5. Then $Al(NO_3)_3{\cdot}9H_2O$ (analytical grade, Merck, Germany) powder was added slowly to the solution under stirring down to pH 8. Using sodium hydroxide pellets, the pH of the solution was adjusted to the final value of 10. The obtained suspension was transferred into a Teflon-lined stainless steel autoclave to fill 85% of the total volume. The autoclave was sealed and maintained at 120 °C for 24 h under autogenous pressure. Then the autoclave was allowed to cool to room temperature. The obtained white precipitate was filtered through centrifugation, washed with distilled water and ethanol several times, and dried in an oven at 50 °C for 12 h.

The crystalline phase of the obtained powder was characterized with X-ray diffraction (XRD) analysis (XRD, Siemens D500 Diffractometer) between 2θ of 10°–80°, and the pattern was plotted after α_2-stripping. The morphologies and nanostructures were determined with a 200 keV transmission electron microscope equipped with a field emission gun (FEG-STEM, Philips CM200) and scanning electron microscope (SEM, Philips XL30).

3. Results and discussion

The XRD pattern of the produced sample using Cu-Kα radiation is shown in figure 1. From the XRD analysis, the produced powder is AlOOH with an orthorhombic type structure (JCPDS card No. 21-1307).

Fortunately, no evidence could be found for the existence of impurities in the product after washing, which may be due to a complete reaction that occurred during the synthesis.

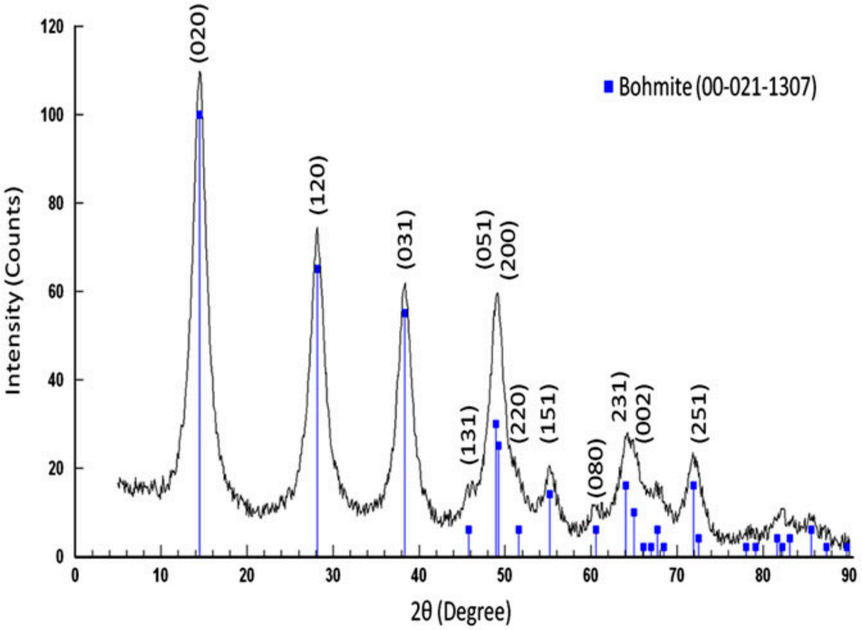

Figure 1. XRD pattern of powder and an identified phase.

According to estimation of the Scherrer's formula [35], the average crystallite size of the obtained boehmite powder was about 2.4 nm:

$$D = \frac{0.89\lambda}{\beta \cos(\theta)} \tag{1}$$

where D is the average crystallite size in nm and λ, β, and θ are Cu-Kα wavelength (0.1540 nm), full width at half maximum intensity of the (020) peak in radians and Bragg's diffraction angle, respectively.

Transition electron microscopic (TEM) images of the synthesized bohemite, as shown in figure 2, reveal that the AlOOH nanocrystals self-organize themselves into flower-like assemblies. The assemblies may be induced by the interaction between nanostrips during the hydrothermal process. These results are in accord with research performed by Zanganeh *et al.* [23], who have studied the boehmite nanostructure. Figure 3 shows a 3-D flower-like nanoarchitecture with average width of 100–150 nm. Figure 3(b) shows a representative high-magnification TEM image of the nanostrips, which allows us to determine their length of 100–200 nm and thickness of 20–70 nm. From the observed morphologies of the products at different evolutionary stages, we proposed the mechanism of formation based on the effect of TEA on the flower-like formation of the nanostructures (figure 3). The use of surfactants as stabilizers has advantages with the fact that these surface-active chemicals possess sufficient strength to effectively control particle size growth. The surfactants assist for particles with uniform size distribution and increased aspect ratio, and they also prevent the particles from agglomeration [36–38]. In the current experiment, the addition of TEA in the reaction has a considerable effect on the morphology of the crystals during the growth from the precursor solution [43]. During the first step of the experiment, addition of $AlCl_3$

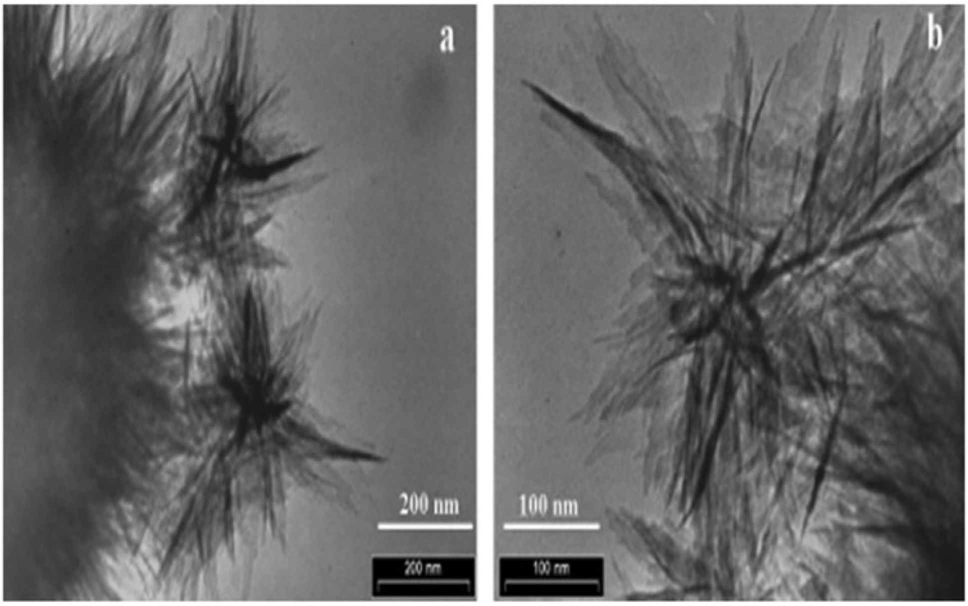

Figure 2. TEM images of boehmite nanostructure synthesized (a) flower-like image of the powder and (b) high magnification image.

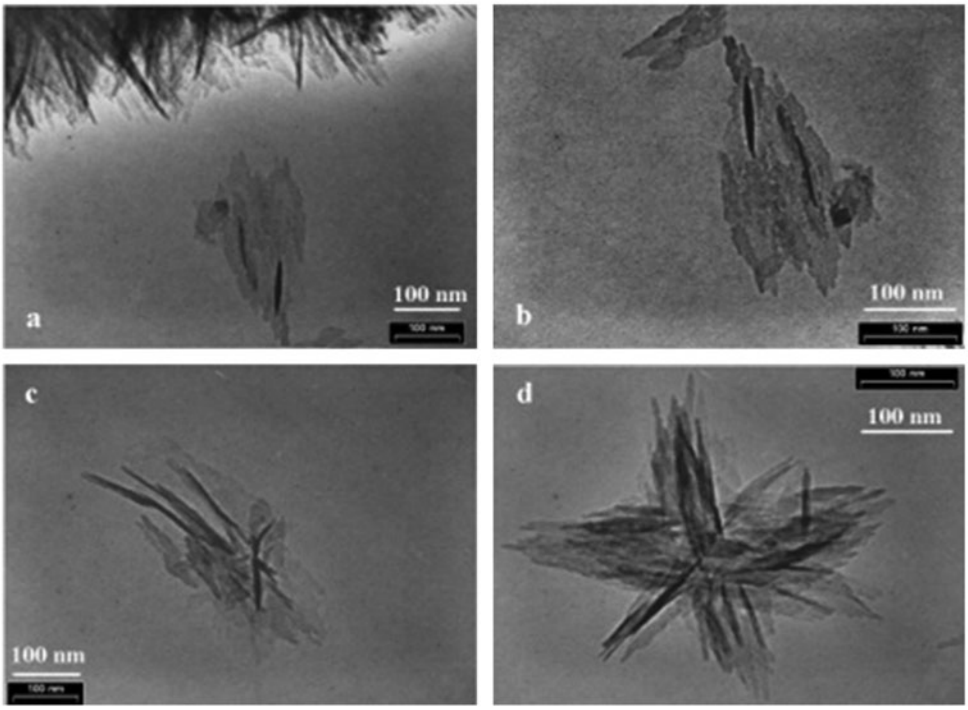

Figure 3. TEM images of nanoboehmite formation (a) nanostrips (b) and (c) the first self-assembly of nanostrips and (d) the second self-assembly.

powder to aqueous solution of triethanolamine (TEA) resulted in dissolution of the solid crystals and formation of Al-TEA complexes as follows:

$$AlCl_3 + TEA\,(aq.) \xrightarrow{stirring} Al\text{-}TEA + 3Cl^- \quad (2)$$

In principle, the formation of the 3-D structure can be divided into two processes, i.e. nucleation and growth. Based on reaction (2), the released chloride ions ($3Cl^-$) decreased the pH of the solution to nine. Under this condition, the aqueous environment culminated in hydroxylation of aluminum ions, and formation of gibbsite $Al(OH)_3$ colloidal nanocrystals is due to the chemical stability of this compound at pH 9 [39]. The $Al(OH)_3$ colloidal nanocrystals provided preferential sites for growth and assembly of the final architecture.

In solution synthesis, surfactant or additive is commonly used to regulate size and shape of inorganic–organic crystals [40, 41]. Li *et al.* demonstrated that toluene added to solvent has a significant effect on the morphology and formation of the boehmite [42]. Therefore, it is suggested that TEA can be adsorbed to modify the growth of crystals only on certain crystallographic planes of the gibbsite growth units formed in solution. Furthermore, as indicated, Cl^- ions can affect growth morphology as well. Zanganeh *et al.* [23] reported that the presence of Cl^- ions in solution favors anisotropic growth of nanocrystals and results in formation of strip-like clusters. Adding CH_3COONH_4 to the aforementioned solution [equation (2)] can create two ions which exist in the following equilibrium (3).

$$CH_3COONH_4 \rightarrow CH_3COO^- + NH_4^+ \tag{3}$$

According to the boehmite crystal system (i.e. orthorhombic), two parallel octahedral layers through a hydroxyl group have been connected. Indeed, oxygen ions are arranged in a distorted octahedral configuration around aluminum and organized in parallel layers linked by hydrogen bonds [44]. Therefore, individual boehmite nanostrips self-assemble laterally due to the surface hydrogen bonds and form bundles of boehmite nanostrips. Also, NH_4^+ ions are effective for the growth mechanism. According to figure 3(d), bundle-formation of self-assembled boehmite nanostrips can be related to adsorbed ammonium ions on the surface of the nanostrips, which assist their connection via H-bonding. Here, the bonding between TEA groups, and nanostrips absorbed NH_4^+ ions with surface hydroxyl groups of each boehmite layer, decreases significantly the tendency of interlayer stacking through hydrogen bonds.

After addition of the nitrate-based aluminum compound to the solution, nitrate ligands interact with the TEA groups on the surface of the gibbsite anisotropic clusters due to weak intermolecular absorptions. Under hydrothermal conditions, such interactions are agents for self-assembly of the anisotropic nanoclusters to form a 3-D architecture. The activation energy for such behavior is the reduction of surface free energies [23, 45]. In addition, under hydrothermal conditions, the gibbsite phase can easily be decomposed to boehmite as follows:

$$Al(OH)_3 \rightarrow AlOOH + H_2O \tag{4}$$

Figure 4 displays schematically nanoboehmite formation through a two-step self-assembly. The first scheme represents how nanostrips make bundles by assembly and finally, bundles through the second assembly generate a flower-like nanostructure.

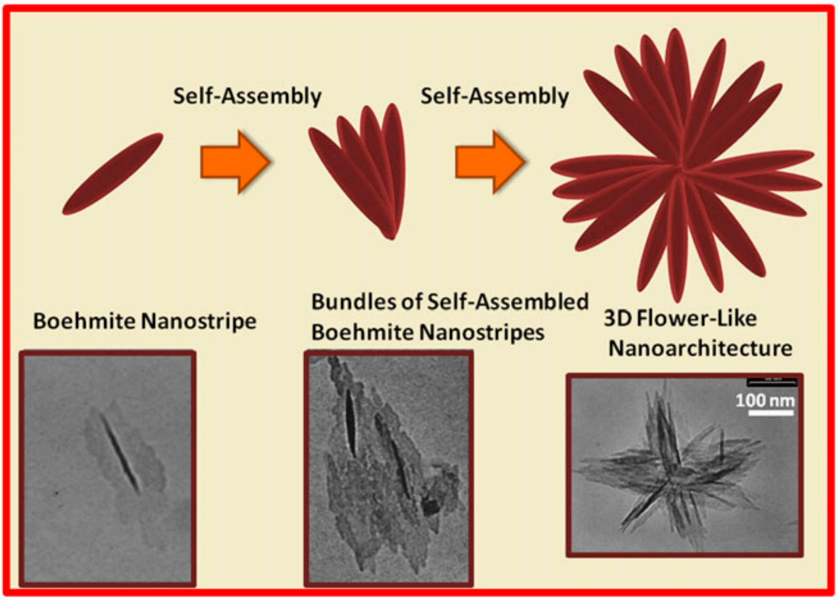

Figure 4. Schematic formation of nanoboehmite by hydrothermal method.

Studies on the specific surface area and porous nature of the boehmite nanopetals were carried out by a Brunauer–Emmett–Teller (BET) gas-sorption measurement. The BET specific surface area of the sample calculated from the N_2 isotherm at 77 K was 160 $m^2 g^{-1}$. In fact, the AlOOH nanopetals acquired in this study have an extremely high BET area, making them promising candidates for technical applications as sensors, catalysts, optical nanodevices, and absorbents. The enlarged surface area is a key advantage of nanomaterials. As a result, surface modification is a very important aspect in the use of nanomaterials in biomedical applications [46]. Xu *et al.* have synthesized 3-D, flower-like boehmite on a large-scale via a surfactant-assisted hydrothermal process. Nitrogen adsorption/desorption measurements indicated that hierarchical AlOOH architectures had a BET surface area of 70.1 $m^2 g^{-1}$ [47]. Zhu *et al.* prepared boehmite particles by a sol–gel method as a robust carrier for enzyme encapsulation. These particles showed relatively high BET surface area of 150 $m^2 g^{-1}$, which is close to our results. They believe that this high surface area may endow these boehmite particles with good characteristics as a carrier for enzyme encapsulation [48]. In general, the surface area of nanorods and nanoparticles are much lower than 3-D nanostructures and based on the literature, this number varies from 5 to 100 $m^2 g^{-1}$ [49, 50].

4. Conclusion

Using a hydrothermal method, flower-like nanoboehmite with an average width of 100–150 nm was prepared. The nanoarchitectures consisted of nanostrips with average lengths between 100 and 200 nm and average crystallite size of 2.4 nm. The formation mechanism was proposed based on binary self-assembly of nanostrips and nanobundles as a result of Cl^- ions, TEA, and NH_4^+ in the precursor solution. The specific surface area of the obtained boehmite was more than 160 $m^2 g^{-1}$, which shows the high surface area of the structure due to its three-dimensionality and nanosized bundles.

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