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The self-assembly of twinned boehmite nanosheets into porous 3D structures in ethanol–water mixtures

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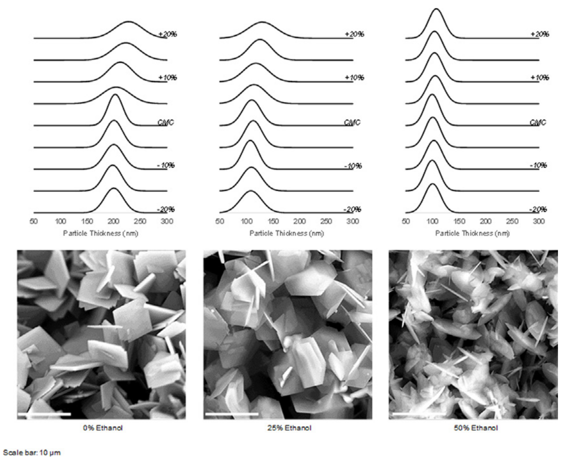
HIGHLIGHTS

- Twinned boehmite nanosheets with uniform shape/thickness were formed.
- Superstructures in 50 vol% ethanol were 2× thinner than in pure water.
- Superstructures in 50 vol% ethanol were 13× more permeable than in pure water.
- Integrity of the 3D porous network was maintained upon filtration.
- Control over thickness of nanosheets is lost above CMC of surfactant.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfactant molecules have high surface activity, and can therefore influence the self-assembly of nanomaterials. The self-assembly of twinned boehmite nanosheets into porous 3D superstructures will be greatly affected by the presence of surfactant monomer and micelles in various ethanol–water mixtures. It should be possible to influence the shape, thickness, and twinning of boehmite nanosheets by varying the concentration of the surfactant and ethanol in the synthesis mixture to obtain high porosity 3D superstructures.

Experiments: The critical micelle concentration (CMC) of cationic surfactant cetyl trimethylammonium bromide (CTAB) was determined in 0, 12.5, 25, 37.5, and 50 vol% ethanol–water mixtures. The effect of CTAB on boehmite particle morphology and superstructure formation during self-assembly was explored at the CMC, and at 20%, 15%, 10%, 5% below and above the CMC of CTAB in various ethanol–water mixtures.

Findings: Boehmite nanosheets with controllable shape and thickness were successfully formed in various ethanol–water mixtures. Prior to micelle formation, the average thickness of nanosheets formed in 0 vol%, 25 vol%, and 50 vol% ethanol–water were 200 nm, 110 nm and 100 nm, respectively. Micelle formation reduced the availability of surfactant molecules for particle templating, broadening the nanosheet thickness distribution. Micelle formation was inhibited in 50 vol% ethanol–water due to the increase in Gibbs free energy needed to form micelles relative to the Gibbs free energy of micelles in 0 vol% or 25 vol% ethanol–water. The enthalpy-driven process gives greater control over the nanosheet thickness, producing particles with narrow thickness distributions. In general, the CMC represented the point at which control is lost over the thickness of the nanoplatelets; increasing the surfactant concentration above the CMC increased the thickness of the nanoplatelets.

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Particle twinning during crystal growth produced an interconnected 3D network of boehmite particles with high porosity (79–88%) and hydraulic permeability (62.4–809 mD). The addition of ethanol during synthesis increased the porosity and reduced the bulk density of the 3D superstructures by 8–11% and 26–28%, respectively, and yielded a ten-fold increase in the hydraulic permeability. The integrity of the porous 3D network was maintained upon calcination, suspension in water and deposition by filtration onto cellulose filter paper.

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1. Introduction

Particles with controlled morphology are of increasing interest in the field of materials science. Shape-controlled particles find use in catalysis [1–3], imaging [4–7], medical therapy [6–9], SERS [10–13], and photovoltaic devices [14,15].

The use of surfactants to control particle morphology has been previously explored [16–22]. At sufficiently high concentration, surfactant monomers self-assemble into well-defined shapes with high surface activity, giving them the ability to direct material synthesis.

Boehmite (γ-AlOOH) is a naturally-occurring aluminum oxide hydroxide crystalline mineral that can be synthesized from organic or inorganic precursors [23,24]. Calcination transforms boehmite into various alumina phases, increasing the material strength. Boehmite and dehydrated alumina powders possess a high surface area and a negative surface charge, making them ideal for applications as adsorbents [25–30] and catalyst supports [31–34]. Thickness and shape-controlled alumina platelets are used in the manufacturing of substrate-based special effects pigments. These pigments require alumina flakes with narrow thickness distributions and smooth finishes [35,36].

The effect of surfactants on boehmite and alumina particle morphology has been explored in the literature. Zhang et al. formed non-porous cantaloupe-like boehmite superstructures using mixtures of aluminum nitrate and high concentrations of aqueous CTAB [37]; Mathieu et al. formed aggregated platelets and long nanofibers by varying the synthesis time using a high concentration of aqueous sodium polyacrylate and aluminum chloride [38]; Liu et al. synthesized boehmite and alumina nanoleaves and non-porous 3D superstructures from aluminum chloride in 50% ethanol–water mixtures [39]; Kuang et al. formed aggregated boehmite and alumina nanotubes via a hydrothermal route in aqueous CTAB solutions using aluminum chloride [40]; Bleta et al. explored the effect of calcination temperature, precursor concentration, and the CMC of Plurionic F127 on the morphology of aggregated alumina nanofibers formed from aqueous aluminum tri-*sec*-butoxide solutions [41]. In all these studies, boehmite and alumina particles were synthesized as aggregated particles, fibers with high anisotropy or 3D structures that lacked internal porosity. In general, these building blocks form superstructures with anisotropic hydraulic permeability that consolidate or collapse when used as a filter [42,43]. Instead, it is desired to form homogeneous, uniformly-structured building blocks from boehmite that will link together to form rigid, highly isotropic, porous 3D superstructures that do not collapse upon deposition on a substrate or during filtration.

In this work, the effect of ethanol content on the critical micelle concentration (CMC) of a cationic surfactant was assessed. Then, the effect of surfactant concentration and the effect of micelles on the shape, thickness, and twinning of boehmite particles during particle self-assembly was determined in 0, 25, and 50 vol% ethanol–water mixtures. The synthesis conditions at which porous 3D superstructures could be formed were determined. Particle characterization was performed via SEM, FTIR, XRD, and image analysis.

2. Experimental

2.1. Materials

Cetyl trimethylammonium bromide (CTAB), sodium hydroxide pellets and anhydrous ethanol were purchased from Sigma–Aldrich (Switzerland). Aluminum chloride hexahydrate (99%, nitrogen flushed) was purchased from Acros Organics. Cellulose filter paper (Whatman #1) was purchased from Fisher Scientific (Canada). All materials were used as purchased.

2.2. Methods

2.2.1. Conductometry studies

The critical micelle concentrations of CTAB were determined in 0, 12.5, 25, 37.5, and 50 vol% ethanol–water mixtures via conductometric analysis at 298 K. A typical procedure was as follows: 250 mL of distilled, deionized water and known masses of CTAB were slowly added and stirred in a beaker. After each addition of CTAB, the conductivity of the solution was measured using a conductivity meter (VWR sympHony B40PCID, Pennsylvania). The measurements were performed in triplicate.

2.2.2. Particle synthesis

Boehmite nanosheets were synthesized via metal salt hydrolysis. A typical procedure was as follows: 1.45 g of aluminum chloride hexahydrate was dissolved in distilled, deionized water under vigorous stirring. The pH of the solution was raised to 14 using sodium hydroxide pellets. CTAB was dissolved in anhydrous ethanol or distilled, deionized water. The surfactant solution was added to the precursor solution and was left to stir at room temperature for 24 h. After spinning, the mixture was poured into a Teflon-lined stainless steel autoclave (Parr Instrument Company, Illinois), sealed, and heated to 165 °C for 12 h under autogenous pressure. The vessel was then left to cool at room temperature overnight. The precipitate formed during crystallization accumulated at the bottom of the autoclave in the form of a rigid disk. The disk of particles was placed in a fume hood to dry. It was then covered and stored for analysis.

2.2.3. Particle characterization

Particles were mounted on aluminum stubs (Ted Pella, Redding, California). SEM imaging was performed using a JEOL 6610LV SEM at accelerating voltages of 10 and 20 kV (Japan Electron Optics Laboratory, Massachusetts) and a Phenom Pro Desktop SEM (Nanoscience Instruments, Virginia) at accelerating voltages of 5 and 10 kV. Particle thickness was determined by measuring the thickness of 20 nanosheets at each synthesis condition using ImageJ software. The data were then fitted to normal distribution curves using Microsoft Excel. FTIR analyses of the particles were conducted using a Cary 630 FTIR with ATR (Agilent Technologies, Canada). Powder X-ray diffraction (XRD) analysis was carried out at room

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