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Colloids and Surfaces A: Physicochemical and Engineering Aspects

Synthesis method for crystalline hollow titania micron-cubes

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HIGHLIGHTS

- A straightforward synthesis method for cubic titania colloids is presented.
- The synthesis method only requires conventional chemicals and ambient conditions.
- Hollow and core–shell hematite@titania colloids are prepared.
- The cubic shape allows for the formation of dense colloidal arrays.

GRAPHICAL ABSTRACT
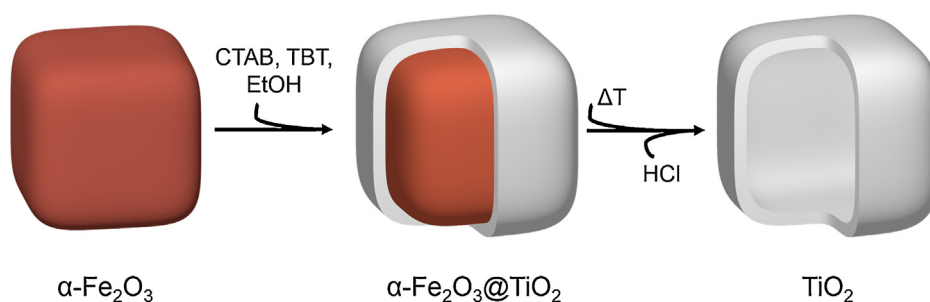
ARTICLE INFO

ABSTRACT

We report the synthesis of novel micron-sized titania cubes comprising a hematite core and a titania shell. Single core particles are entirely coated with a homogeneous titania shell of tunable thickness. Our convenient and straightforward synthesis method is mediated by the surfactant cetyltrimethylammonium bromide (CTAB) and proceeds under ambient conditions. Subsequent calcination transforms the amorphous titania shell to anatase/rutile titania; dissolution of the hematite core eventually results in hollow porous titania cubes. The resulting core–shell and hollow titania cubes display the tendency to align face-to-face, indicating their potential for utilization in close-packed arrays.

1. Introduction

Titania particles are widely applied, e.g., as pigments [1,2], photocatalysts for degradation of organic compounds and for water-splitting [1,3–5], and components in photovoltaic devices [1,6–8]. Moreover, the mechanical and chemical robustness of titania contribute to its extensive use in ceramics, such as separation membranes [9,10]. Another emerging application of titania colloids lies in the field of photonic materials [11,12]. For especially the latter two applications, dense packings of colloids are of interest. Such particle packings are generally composed of spherical particles, resulting in a maximum volume fraction of circa 0.74 [13,14]. An increased volume fraction, on the other hand, can be obtained with more cube-shaped particles, up to 1 for perfect cubes [13,14]. Recently, the formation of dense arrays using colloidal cubes composed of silica and hematite has been demonstrated [15–18]. Due to the slightly rounded corners of the employed particles, the

maximum volume fraction that could be achieved was circa 0.87 [13,14]. Although not a perfectly dense packing, the achieved volume fraction was substantially higher than for spheres. In a similar way, it would be relevant to have such dense assemblies composed of titania building blocks as to combine the advantages of dense particle packings and the material properties of titania. As a first step towards this aim, we present here a convenient synthesis method for colloidal titania cubes.

Many of the listed applications actually only require titania at the surface of the particles, such that core–shell particles with a titania shell suffice. Unfortunately, the synthesis of titania coated colloids is notoriously challenging due to fast hydrolysis and condensation reactions of titania alkoxide precursors [19,20]. Therefore, numerous procedures employ titanium complexes as precursors [21,22], special stabilizers [23] or solvent mixtures [20,24] which retard reaction rates, but, unfortunately, at the same time complicate the synthesis. As an alternative to these procedures, we report a straightforward and reproducible synthesis method for titania shells grown directly onto micron-sized, cubic hematite (α-Fe$_2$O$_3$) cores. Titania growth occurs here at ambient conditions and with the use of the conventional titania precursor titanium(IV) butoxide (TBT) and as mediator, the surfactant cetyltrimethylammonium bromide (CTAB). Our procedure results in core–shell hematite@titania cubic colloids, which can subsequently be transformed to stable anatase/rutile titania cubes and which can even be made hollow by dissolution of the hematite cores. Notably, our method results in the formation of titania shells around single particles and aggregation is generally avoided. Eventually, the titania cubes could serve as building blocks of dense particle assemblies.

2. Materials and methods

2.1. Particle synthesis

2.1.1. Hematite cubes
Monodisperse cubic hematite particles were prepared following an adapted sol–gel method of Sugimoto et al. [17,25]. Typically, a mixture of aqueous solutions of iron(III) chloride (2.0 M, iron(III) chloride hexahydrate, p.a., Sigma–Aldrich) and sodium hydroxide (5.4 M, p.a., Emsure) was aged at 100 °C for eight days. The resulting sol was then washed by centrifugation and redispersion in Millipore water until pH ~7 was reached. Bigger cubes can be obtained by using a larger excess of iron(III) ions.

2.1.2. Core–shell hematite@titania cubes
The synthesis of titania coated hematite cubes is mediated by the surfactant cetyltrimethylammonium bromide (CTAB, 99%, Sigma–Aldrich) and typically proceeds as follows. Firstly, a mixture of 1.7 g (dry weight) hematite cubes and 420 mL aqueous CTAB solution (1.7 mM) was sonicated for 1 h. Secondly, an ethanolic titania precursor solution was made in a glovebox by mixing 4.5 g titanium(IV) butoxide (TBT, reagent grade 97%, Sigma–Aldrich) with 67.5 mL absolute ethanol (Merck). Subsequently, the following was added at ambient conditions to a 1 L round bottom flask while sonicating at 20 °C: 360 mL absolute ethanol, 15 mL Millipore water and the cubes/CTAB mixture. Next, 67.5 mL of the TBT solution was quickly added with a dropping funnel. The reaction mixture was then sonicated for an additional 8 min after which it was washed five times by centrifugation and redispersion in ethanol. To ensure all titania aggregates resulting from secondary nucleation were removed, a decreasing centrifugation speed was applied in each consecutive washing step: 500 g, 450 g, 350 g, 150 g and 50 g. The cubes were eventually redispersed in 420 mL absolute ethanol. The resulting cubes were then coated again following the

method described above, but without the addition of CTAB. The final sediment was redispersed in 210 mL absolute ethanol.

2.1.3. Calcined and hollow titania cubes
For the calcination process, dried cubes were first heated at 60 °C for 1 h (heating rate 80 °C/h from 20 °C to 60 °C) and then at 450 °C for 3 h (heated from 60 °C to 450 °C in 6.5 h). The thermal treatments were performed in air and with a Nabertherm N15/65 HA oven. The dry calcined particles were redispersed in 30 mL absolute ethanol.

Hollow titania cubes were produced by treating calcined core–shell cubes with hydrochloric acid (6 M, Merck) to dissolve the hematite core. Complete dissolution was marked by a color change of the dispersion from red to yellow, caused by the dissolution of hematite to iron(III) ions and chloride ions. Complete dissolution was typically achieved within a few hours. The dispersion was then washed with Millipore water until pH ~7 was reached. The acid treatment to obtain hollow titania cubes should only be performed on calcined core–shell hematite@titania cubes which have a crystalline titania shell; amorphous titania cannot withstand the acid treatment and dissolves on a time scale similar to the hematite core.

2.2. Characterization

The cross-sectional appearance, average particle size and thickness of the produced titania shells were analyzed with Transmission Electron Microscopy (TEM), see Fig. 2B. The average size was determined from the edge length of at least 100 particles. The coating thickness was calculated by subtracting the average size of the core particles from the average size of the core–shell cubes. TEM samples were prepared by drop-casting diluted dispersion onto a polymer coated, carbon sputtered copper grid and were dried under a heating lamp. The employed Transmission Electron Microscopes were a Philips Tecnai 12 (120 kV) and Tecnai 10 (100 kV). The morphology and surface of the cubes were investigated with high resolution Scanning Electron Microscopy (SEM). SEM samples were made by sticking a TEM sample on a stub using a conductive carbon sticker. The entire SEM sample was then coated with a layer of platinum of typically 6 nm prior to analysis with a FEI XL30 FEG operated at 5–15 kV. With the employed SEM, elemental analysis with energy dispersive X-ray spectroscopy (EDX) of the particles was also performed.

Infrared spectra were recorded with a Perkin Elmer Frontier FT-MIR Spectrometer using KBr pellets as medium.

Wide-angle powder X-ray diffraction (XRD) measurements were performed at room temperature on a Bruker-AXS D2 Phaser Diffractometer using Co Kα radiation (λ = 1.78897 Å) and operated at 30 kV and 10 mA. The employed step size was 0.0991° in the angle range of $15° \leq 2\theta \leq 80°$.

Nitrogen physisorption measurements were performed on a Micromeritics TriStar 3000. The cubes were dried under a nitrogen gas flow prior to measurement, first overnight in a sample concentrator at 60 °C and then further overnight at 180 °C with a Micromeritics Smartprep. The specific surface area was derived by fitting the Brunauer–Emmett–Teller (BET)-isotherm in the linear relative pressure range p/p_0 = 0.06–0.25 of the measured adsorption isotherm. Barrett–Joyner–Halenda (BJH) analysis was performed to determine the pore size distributions [26].

3. Results and discussion

The synthesis of hollow cubic anatase/rutile titania particles comprises four stages. The first stage is the synthesis of hematite (α-Fe$_2$O$_3$) cubes, which act as the shape template. Following [17,25], we synthesize monodisperse hematite cubes, the edge length of which can be varied between 500 nm and 1500 nm. In this study, we employ hematite particles with a highly cubic shape and an