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Silica cubes with tunable coating thickness and porosity: From hematite filled silica boxes to hollow silica bubbles

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ABSTRACT

We investigate the material properties of micron-sized silica coated cubic colloids, focusing on the coating thickness and porosity. The thickness of the silica coating of core–shell α-Fe_2O_3@SiO_2 cubes and their corresponding hollow cubes can be tuned between 20 and 80 nm, spanning the range of silica bubbles to silica boxes. The porosity of the silica cubes can be increased controllably by surface-protected etching using hot water as mild etchant and polyvinylpyrrolidone (PVP) as protecting polymer. We introduce infrared spectroscopy as a quantitative tool to monitor the extent of etching over time and to evaluate the influence of PVP on the etching process. The molar mass of PVP does not affect the etching rate, whereas an increased amount of PVP leads to enhanced protection against etching. Silica etching is found to be a two-step process, comprising a fast initial etching followed by a slower continuation. Hollow, porous silica cubes maintain their shape after extensive thermal treatment, demonstrating their mechanical stability.

1. Introduction

Silica is an inorganic material that has been widely studied, mainly due to its abundance in nature but also because of its many practical applications [1]. The latter is promoted by the many forms and degrees of crystallinity of this chemically and mechanically robust material, and also by the ease of modification and adaptation to the needs of an application. Colloidal solid and core–shell silica particles are often used in paints, coatings, food industry, bio-imaging and drug-targeting [1–9].

In this work, we consider the material properties of recently developed micron-sized, porous silica colloidal particles with a distinct cubic shape. The cubes are either core–shell particles with a hematite core (α-Fe_2O_3) coated with amorphous silica or hollow silica cubes obtained by dissolution of the hematite core. These silica cubes, first reported in [10], are fascinating colloids: their characteristic shape leads to particular phase behavior and allows for the formation of marked architectures, which both can be examined conveniently with conventional microscopy techniques due to the colloidal size of the particles [10,11]. In addition to the structural properties, these porous silica particles are of interest as possible nanoreactors for catalysis or as building blocks for ceramic membranes. Obviously, proper control over the properties of the silica coating is essential for such applications but also for fundamental research on these silica cubes. Unfortunately, such knowledge of these silica cubes is still lacking. Therefore, we directed our research to controlling the thickness and porosity of the silica coating on the cubes while still maintaining their stability.

A smooth and homogeneous layer of Stöber silica is easily grown onto the hematite core by functionalizing it with the polymer polyvinylpyrrolidone (PVP) [12]. PVP is an amphiphilic, non-ionic polymer that readily adsorbs onto a wide range of materials and is regularly employed as a stabilizer [12–18]. The formation of Stöber silica is based on the base-catalyzed hydrolysis and condensation of the silica precursor tetraethoxysilane (TEOS). The resulting silica is amorphous and porous, caused by incomplete cross-linking of siloxane bonds [1,19–21]. The thickness of the silica coating is varied by suitably adjusting the amount of silica precursor [9,12,22]. The synthesis route is schematically depicted in Fig. 1.

To increase the porosity of the already intrinsically porous Stöber silica further, we make use of surface-protected silica etching. The procedure involves the adsorption of a surface polymer to the silica which protects the outer layer of the silica structure

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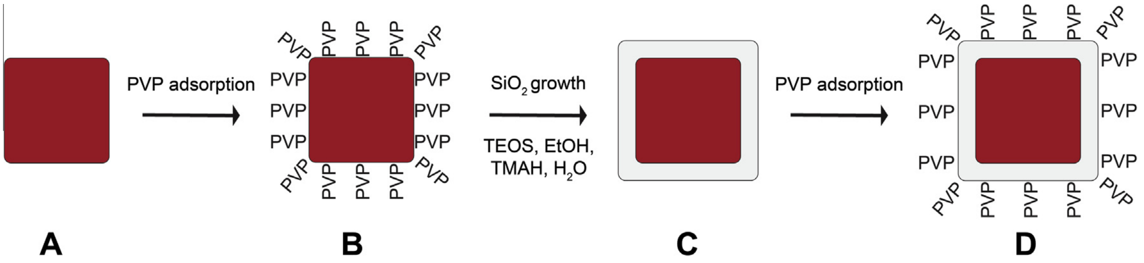

Fig. 1. Schematic illustration of the synthesis of silica coated iron oxide cubic colloids. Polyvinylpyrrolidone (PVP) is first used as a coupling agent between the seed particle (A) and the silica coating (B) and then as stabilizing and protecting polymer (D) on the silica coated iron oxide cube (C).

against etching, resulting in a porous interior [16,18,20,23]. To have better control over the etching process, we employ water at elevated temperature, which is a mild etching agent [1,21,24,25]. Contrary to previous research, we quantify the extent of etching using infrared spectroscopy with the hematite core as internal standard, and we discuss the effect of the protecting polymer [16,18,20,23]. In view of employing the particles in ceramic materials, we also relate the change of the properties to the mechanical strength upon heating.

2. Experimental

2.1. Chemicals

All chemicals were used as received and were stored at ambient conditions. The hematite (α-Fe_2O_3) cubic colloids were prepared as described in [10,26,27] and stored in Millipore water. Millipore water (pH 5–6) obtained from Synergy Ultrapure Water Systems was used for all aqueous systems. Technical ethanol (100%, Interchema) was used as solvent in both the synthesis and the etching of the silica coating. Absolute ethanol from Merck was used as solvent only when indicated. Polyvinylpyrrolidone (PVP) 10 kg/mol and 40 kg/mol and tetramethylammonium hydroxide (TMAH) 25 wt% were purchased from Aldrich and Sigma–Aldrich, respectively. Tetraethoxysilane (TEOS) purum and potassium bromide for IR spectroscopy were both obtained from Fluka. Hydrochloric acid (37 wt%, fuming) was purchased from Merck.

2.2. Silica coated hematite cubes

The synthesis procedure for the coating of cubic hematite colloids with silica and the subsequent removal of the hematite core is based on the procedure described by Rossi et al. [10]. A detailed description of these procedures is given in the Supplementary information. Here, we note the alterations compared to the method of Rossi et al.

For both the functionalization and stabilization of the cubic particles, PVP was adsorbed to the particles. In both cases, we used PVP with a molar mass of 40 kg/mol instead of the 10 kg/mol PVP used by Rossi et al. Moreover, we reduced the reaction volume to half of the original volume by reducing the amount of ethanol, while keeping the other reactant amounts the same. We observed that this reduction did not affect the results. Lastly, the dye solution of rhodamine B isothiocyanate and 3-aminopropyltriethoxysilane (APS) was omitted and replaced by an equal amount of TEOS solution. The dye was required for the visualization of the cubes with confocal microscopy, a technique that was not employed in this study.

The hematite core of the silica coated hematite cubic colloids can be removed by dissolving it with a 6 M hydrochloric solution. The dissolution of the hematite core is accompanied by a color change of the dispersion from red to yellow, caused by the formation of dissolved iron ions. Complete dissolution occurred in typically 24 h, after which the mixture was washed with ethanol to remove all acid. The time required to dissolve the entire core, however, depends on the thickness of the silica coating, the size and the concentration of the cubes.

2.3. Surface-protected etching of silica

The cubic colloids used for the silica etching experiments still contained their hematite core. The hematite core was used as an internal standard for the infrared (IR) spectroscopy measurements, since the amount of hematite is not affected by the etching process. Accordingly, the decrease of the amount of silica can be quantified when the peak of silica is normalized to the hematite peak, as explained in Section 2.5. For more control over the etching process, we used water at elevated temperatures as mild etching agent. The solubility of amorphous silica greatly increases at elevated temperatures, rising from ~140 ppm at 22 °C to ~300 ppm at 73 °C, both measured at pH 7 [1,24]. For a typical silica etching procedure, first a PVP solution was prepared by completely dissolving in a three-neck round bottom flask 1.1 g PVP in 20 mL freshly tapped water by magnetic stirring, followed by sonication for 15 min. This solution was then heated to 85 °C using an oil bath on a heating plate while refluxing and stirring magnetically. Second, an aqueous dispersion of silica coated hematite cubes (11 g/L), initially stored in ethanol, was prepared by centrifugation and redispersion in water. As soon as the PVP solution reached 85 °C, 10 mL of aqueous dispersion was added in batches of 2–4 mL. The reaction mixture was stirred vigorously while maintaining the heating and refluxing. Upon addition of the cooler dispersion to the PVP solution, the temperature dropped but quickly reached the set temperature of 85 °C again. The etching time started once all aqueous dispersion had been added. Aliquots were extracted at given times using a Finn pipette. The extracted samples were transferred to a centrifuge tube and cooled immediately to room temperature with cold tap water. The sample with the longest etching time was cooled gradually by the removal of the heating plate. The samples were diluted with ethanol before they were washed five times with ethanol. Typically, the sols were centrifuged at 1000g for 35 min. per cycle to remove the PVP and dissolved silica still present after the etching process and maintain only the silica cubes. The resulting etched cubes were finally stored in absolute ethanol. To determine the effect of the molar mass and amount of PVP on the results, variations on the above-described procedure were conducted and are listed in Table 1.

2.4. Heat treatment of silica cubes

In view of the potential application of the silica cubes in ceramic materials, it is relevant to gain insight into their stability after thermal treatment. Therefore, mica substrates of 5 × 5 mm were completely covered by a 10–30 µL droplet of hollow silica cubes in ethanol. Mica was used because of its smooth surface after cleaving and its good heat resistance. For the sample preparation,