JOURNAL OF Materials CHEMISTRY Communication

Formation of uniform and monodisperse zincite crystals in the presence of soluble starch

Andreas Taubert*† and Gerhard Wegner

Max-Planck-Institute for Polymer Research, D-55128 Mainz, Germany.
E-mail: taubert@seas.upenn.edu

Received 13th November 2001, Accepted 27th January 2002
First published as an Advance Article on the web 15th February 2002

A novel procedure for the formation of uniform, monodisperse, and single-phase zincite particles using soluble starch as crystallization additive is reported. At low starch concentrations, roughly spherical particles with a bimodal size distribution form. At high starch concentrations, the precipitate only contains large, approximately spherical particles with a monomodal and narrow size distribution. A simple precipitation–aggregation mechanism is postulated for particle formation.

Inorganic materials of a specific size and shape are key components in much of the latest technology, including advanced catalysis and semiconductors. Well-defined inorganic powders have been synthesized *via* different synthetic routes. Recently, precipitation from solution has been explored with respect to its capability to yield uniform and monodisperse inorganic powders. Partly due to the conscious effort to eliminate organic solvents from technical processes, precipitation from aqueous solution has come to dominate this field in the immediate past.

It has recently been shown[1–6] that water-soluble polymers are powerful tools for controlling particle shapes, sizes, and size distributions, and thus may be used to tailor inorganic precipitates for specific applications. However, since the synthesis of specific polymeric additives often requires elaborate procedures such as anionic polymerization, a large synthetic effort must be undertaken if a large amount of a specifically designed polymer for particle production on an industrial scale is desired. Alternative sources of additives for particle formation control are thus of interest for large-scale powder synthesis.

Carbohydrates are available in large quantities and can easily be modified and transformed to other products. As a result, an increasing part of industrial and academic research has been devoted to the exploration of carbohydrates and related biopolymers as substitutes for petrochemical-based materials.[7–9] Only a few authors have, however, reported studies on carbohydrate-controlled precipitation of minerals.[10–18] Due to their water-solubility, simple chemical modification, and their availability, carbohydrates should be attractive candidates as crystal modifiers for a wide variety of inorganics. Previous studies investigating the effect of carbohydrates on mostly the precipitation of iron hydroxides and oxyhydroxides involved additional steps such as sterilization,[14] pH adjustments or buffering of the reaction solution,[11–13,15,17] or an argon or nitrogen atmosphere.[17] Here, we report a novel procedure for the formation of monodisperse, uniform, and single-phase zinc oxide particles based on the use of soluble starch as crystallization controlling agent. In contrast to the earlier experiments, our procedure does not require further purification steps or adjustments of the reaction environment. The particles consisted of crystalline zincite and the size distributions of the particles could be fine tuned *via* the additive concentration.

In a typical crystallization 446 mg (1.5 mmol) of $Zn(NO_3)_2\cdot6H_2O$ (Fluka) and 22 mg of soluble starch (Aldrich) were dissolved in 100 ml of deionized water. The solution was refluxed at 100 °C until a slightly opalescent solution was obtained. The solution was cooled to 90 °C and 210 mg of hexamethylene tetramine (HMT, Fluka) dissolved in 2 ml deionized water were added to the slowly stirred solution. HMT slowly decomposes at 90 °C and forms ammonium hydroxide, which induces precipitation by slowly increasing the pH of the solution, and formaldehyde.[19,20] HMT was used instead of NaOH solutions or aqueous ammonium hydroxide solutions to avoid high local supersaturations when the base was added and to achieve a more homogeneous nucleation process. After 90 minutes at 90 °C, the reaction flask was cooled in an ice bath to terminate the reaction. The white precipitate was isolated by centrifuging the suspension and decanting the supernatant liquid. The precipitate was washed several times with water and ethanol and subsequently dried in a vacuum oven at 60 °C for two days.

Scanning electron microscopy‡ (SEM) of the sample precipitated without starch (further referred to as the control sample) found large hexagonal prismatic crystals and very thin needle-like particles (Fig. 1a). The small needle-like particles do not exhibit any visible crystal faces whereas the hexagonal shape of the large crystals is consistent with crystalline zincite particles where the long axis is the crystallographic *c*-axis.[6] In the presence of starch, roughly spherical particles are formed after 90 minutes (Figs. 1b and c). At lower starch concentrations, two particle populations with different sizes are found. The smaller particles have a spherical shape, whereas the larger particles are slightly oblong. At higher starch concentration only large particles are found.

A more detailed investigation of the particles (Fig. 1d) shows that the larger ones are possibly formed *via* the aggregation of the smaller spherical particles, because higher magnification images reveal that they are composed of spherical entities of about the size of the small particles visible in Fig. 1b. These spherical particles in turn consist of even smaller subunits with a dimension of ~10 nm. This implies that the large particles may be formed *via* precipitation followed by a step-like aggregation process.

Since polysaccharides are highly aggregated in solution[21] and form complexes with divalent metal ions,[22–25] both of which are due to their high number of coordinating functional groups, it is likely that the majority of the zinc ions is closely associated with the starch molecules (Scheme 1a).§ Therefore nucleation and initial crystal growth may preferentially occur within regions of both high starch and Zn^{2+} concentration, leading to the ~10 nm nanoparticles (Scheme 1b). They

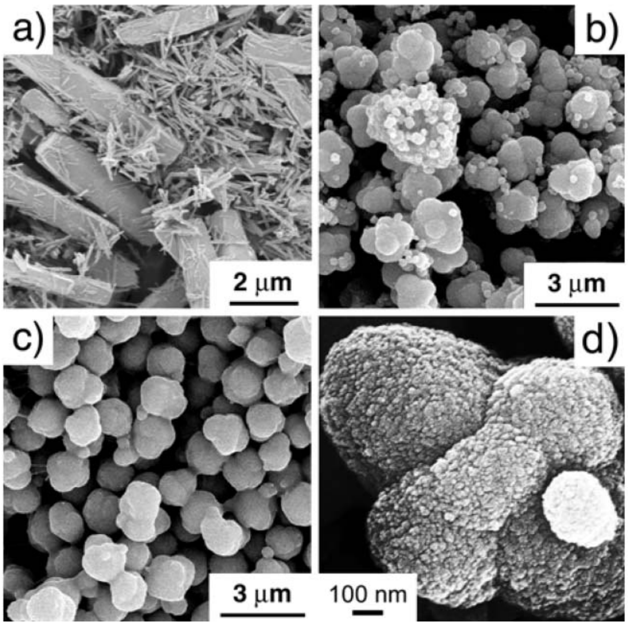


Fig. 1 SEM images of precipitates. a) control sample (no starch), b) sample precipitated with 220 mg l^{-1}, and c) sample precipitated with 960 mg l^{-1} of starch added to the reaction solution, d) higher magnification image of a single particle showing the ~10 nm subunits.

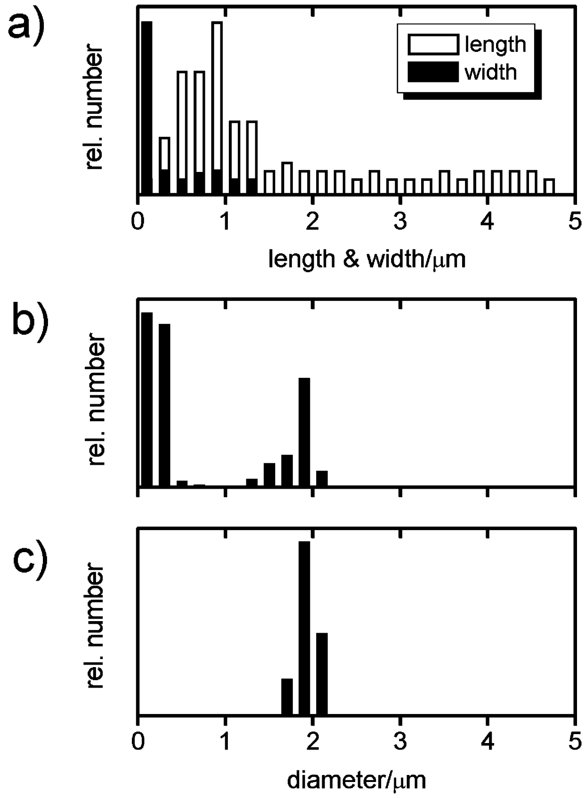
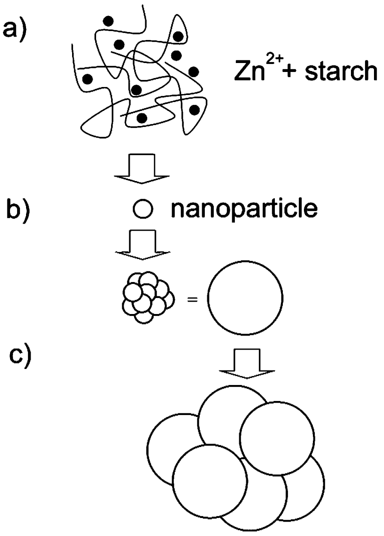


Fig. 2 Size distribution histograms of the samples displayed in Fig. 1. a) Control sample lengths and widths, b) diameters of sample precipitated with 220 mg l^{-1}, and c) 960 mg l^{-1} of starch added to the reaction solution, respectively.

aggregate in a further step and by this process form the small spherical particles. These subsequently aggregate to the large particles (Scheme 1c). The starch presumably acts as flocculant and forces aggregation. This effect becomes more significant at higher polymer concentrations. A similar process has recently been proposed for nanosized TiO_2.[26] While other growth mechanisms are possible, our data as well as work by other authors[18,27–32] make the above presented growth model plausible.

The size distribution of the control sample is very broad (Fig. 2a) with a maximum at *ca.* 1 µm length and *ca.* 100 nm width. At lower starch concentrations, the size distribution of the sample is clearly bimodal (Fig. 2b). The distributions of both individual groups in the histogram of this sample are narrow compared to the control sample. At higher starch concentrations, no small particles are formed, but the size distribution becomes monomodal and narrow (Fig. 2c). Mean diameters¶ obtained for the sample precipitated with 220 mg l^{-1} were 0.19 µm and 1.96 µm, whereas for the sample precipitated with 960 mg l^{-1} an average size of 1.93 µm was found. The large particles therefore have the same size within the experimental error, even if the polymer concentration is changed by a factor of over four. This finding and the fact that the formation of the small particles is suppressed at higher starch concentrations support the assumption that nucleation and initial crystal growth both occur within the associated starch molecules and that the starch favors nanoparticle aggregation followed by aggregation of these nanocrystal aggregates.



Scheme 1 Proposed particle formation. a) Zn^{2+} (black dots) is closely associated with starch (lines). b) Nanoparticles precipitate, aggregate, and form small particles (large circle). c) Small particles aggregate and form large particles. Starch molecules are omitted for clarity in the lower part of the scheme.

Powder X-ray diffraction|| confirmed the formation of crystalline zincite. No other phases were found. The crystallite sizes calculated from the line broadening were ~100 nm for the control sample, which is usually considered to be the largest crystallite size detectable *via* line broadening.[33,34] Crystallite sizes for the two starch-containing samples were 31 nm for the sample precipitated at low and 24 nm for the sample precipitated at high starch concentration. The crystallite sizes of the particles precipitated in the presence of starch may thus correspond to the ~10 nm features seen in the SEM images (Fig. 1d). This again is an indication that a multi-step process leads to the particles obtained with the starch additive.

It is interesting to note that starch plays a completely different role in the precipitation of zincite from aqueous solution than synthetic copolymers. A series of synthetic copolymers have been investigated with respect to their ability to control zincite particle formation.[6] There, the hexagonal shape of the large crystals in the control sample is always retained at the concentrations used in this work. Spherical particles could only be obtained at polymer concentrations above *ca.* 2000 mg l^{-1}. However, no zincite but only amorphous particles were formed at these concentrations.[35] Thus, the uniqueness of the starch additive lies in its capability to favor the formation of roughly spherical zincite particles. With other polymers either spherical *or* zincite particles were obtained.

Thermogravimetric analysis** confirmed polymer incorporation in the crystals. At 220 mg l^{-1} and 960 mg l^{-1}, a weight loss of $\sim$10 and $\sim$32% was found, respectively, indicating that the amount of incorporated polymer increased with increasing solution concentration. The control sample only showed a minor weight loss of $\sim$2% which is presumably due to water desorption.

Soluble starch is a readily available and cheap crystallization additive for zinc oxide precipitation from aqueous solution. It enables the formation of single-phase zincite particles with a well-defined shape and size distribution that are not otherwise accessible. The starch additive may open new perspectives for the formation of monodisperse, uniform and single-phase inorganic particles based on carbohydrate-controlled precipitation reactions. It can easily be functionalized and may thus be tailored for various inorganic systems or to achieve different sizes and distributions of a given inorganic compound.

Acknowledgement

We thank M. A. Rixman and Dr M. Bockstaller for very useful discussions and M. Steiert for help with X-ray experiments. Reviewer B is also thanked for a valuable suggestion. Financial support from the Federal Ministry of Research and Technology, grant No. 03D0045, is gratefully acknowledged.

Notes and references

†Current Address: Department of Materials Science and Engineering, 3231 Walnut St., University of Pennsylvania, Philadelphia PA 19104-6272, USA.

‡SEM experiments were performed on a JEOL JSM6400F field emission SEM at 20 kV. The samples were deposited on conducting carbon tape and sputter-coated with gold. SEM experiments on unsputtered samples confirmed that the nanometer structure was due to the sample and not to the gold sputtering.

§Burchard[21] pointed out that the solution structure of polysaccharides is highly complex and that the analysis of the experimental data is not trivial. We are currently in the process of determining the molecular parameters (molecular weight, polydispersity, aggregation in solution) of the starch both with and without the Zn^{2+} ions present in the reaction solution. Preliminary viscometry experiments indicate a molecular weight of $\sim 10^6$ g mol^{-1}.

¶All histograms were analyzed by fitting a mono- or bimodal Gauss distribution[36] to the experimental values.

‖Powder X-ray patterns were recorded on a Philips PW1820 using a graphite monochromator, scintillation counter, and CuK$_\alpha$ (λ = 1.5418 Å) radiation. Line profile analysis was performed according to[33] with an NBS (now NIST) zinc oxide standard as reference material.

**TGA was done on a Mettler TG50 in oxygen. The heating rate was 10 K min^{-1} and the temperature range 25 to 900 °C.

1 J. H. Adair and E. Suvaci, *Curr. Opin. Coll. Interf. Sci.*, 2000, **5**, 160.
2 P. Calvert and P. Rieke, *Chem. Mater.*, 1996, **8**, 1715.
3 H. Cölfen and Q. Limin, *Chem. Eur. J.*, 2000, **7**, 106.
4 H. Cölfen and M. Antonietti, *Langmuir*, 1998, **14**, 582.
5 J. M. Marentette, J. Norwig, E. Stöckelmann, W. H. Meyer and G. Wegner, *Adv. Mater.*, 1997, **9**, 647.
6 M. Öner, J. Norwig, W. H. Meyer and G. Wegner, *Chem. Mater.*, 1998, **10**, 460.
7 M. N. V. R. Kumar, *Reactive and Functional Polymers*, 2000, **46**, 1.
8 A. K. Mohanty, M. Misra and G. Hinrichsen, *Macromol. Mater. Eng.*, 2000, **276**, 1.
9 L. R. Lynd, C. E. Wyman and T. U. Gerngross, *Biotechnology Progress*, 1999, **15**, 777.
10 K. K. Makinen, E. Soderling, D. R. Peacor, P. L. Makinen and L. Park, *Calcif. Tissue Int.*, 1989, **44**, 258.
11 F. Jones, H. Cölfen and M. Antonietti, *Colloid and Polymer Science*, 2000, **278**, 491.
12 P. Sipos, T. G. St. Pierre, E. Tombacz and J. Webb, *J. Inorg. Biochem.*, 1995, **58**, 129.
13 F. Jones, H. Cölfen and M. Antonietti, *Biomacromolecules*, 2000, **1**, 556.
14 E. M. Coe, R. D. Bereman and W. T. Monte, *J. Inorg. Biochem.*, 1995, **60**, 149.
15 E. M. Coe, L. H. Bowen, J. A. Speer and R. D. Bereman, *J. Inorg. Biochem.*, 1995, **57**, 287.
16 E. M. Coe, L. H. Bowen, J. A. Speer, Z. Wang, D. E. Sayers and R. D. Bereman, *J. Inorg. Biochem.*, 1995, **58**, 269.
17 K. K. W. Wong, T. Douglas, S. Gider, D. Awschalom and S. Mann, *Chem. Mater.*, 1998, **10**, 279.
18 J. F. Banfield, S. A. Welch, H. Zhang, T. Thomsen Ebert and R. L. Penn, *Science*, 2000, **289**, 751.
19 E. Baur and W. Rüetschi, *Helv. Chim. Acta*, 1941, **24**, 754.
20 A. D. Karpyuk, N. S. Kolayda and A. E. Klyugin, *J. Radioanal. Nucl. Chem.*, 1990, **143**, 61.
21 W. Burchard, *Biomacromolecules*, 2001, **2**, 342.
22 S. K. Wiedmer, A. Cassely, M. Hong, M. V. Novotny and M.-L. Riekkola, *Electrophoresis*, 2000, **21**, 3212.
23 A. Magnani, S. Silvestri and R. Barbucci, *Macromol. Chem. Phys.*, 1999, **200**, 2003.
24 J. A. Rendleman, *Food Chem.*, 1978, **3**, 47.
25 J. A. Rendleman, *Food Chem.*, 1978, **3**, 127.
26 R. L. Penn and J. F. Banfield, *Science*, 1998, **281**, 969.
27 M. Ocana, M. P. Morales and C. J. Serna, *J. Coll. Interf. Sci.*, 1995, **171**, 85.
28 M. Ocana, R. Rodriguez-Clemente and C. J. Serna, *Adv. Mater.*, 1995, **7**, 212.
29 G. H. Bogush, M. A. Tracy and C. F. Zukoski, *J. Non-Cryst. Solids*, 1988, **104**, 95.
30 G. H. Bogush and C. F. Zukoski, *J. Coll. Interf. Sci.*, 1991, **142**, 19.
31 A. Chittofrati and E. Matijevic, *Colloids and Surfaces*, 1990, **48**, 65.
32 A. P. Alivisatos, *Science*, 2000, **289**, 736.
33 L. Sagalowicz and G. Fox, *J. Mater. Res.*, 1999, **14**, 1876.
34 B. E. Warren, *X-ray Diffraction*; Dover: New York, 1990.
35 A. Vuin, in *Diploma thesis*, Fachhochschule Fresenius Idstein, 1997.
36 R. J. Hunter, *Foundations of Colloid Science*, Oxford Science Publications: Oxford, 1986, Vol. 1 + 2.