

## Tailoring of Size and Porosity of TiO<sub>2</sub>-Particles

Stefanie Eiden, Johanna Widoniak

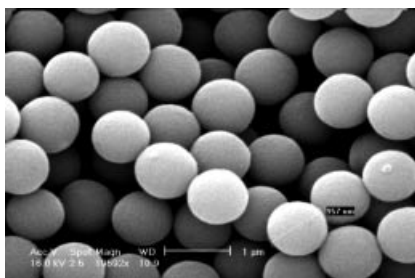
Fachbereich Physik, Universität Konstanz, D-78457 Konstanz

**Keywords:** Colloids; Sol-gel; Synthesis; Titania; Porosity

The importance of well-defined particles has been recognized in a number of applications, for example, in ceramics, catalysis, pigments and, more recently, as building blocks of photonic crystals. Titania particles are particularly interesting with regard to their high refractive index. As titania particles tend to agglomerate they must be stabilized either electrostatically or sterically [1]. In order to investigate the influence of electrostatic and steric stabilization on the formation mechanism, the size and the size distribution of titania particles in more detail, we varied the type of the stabilizing salt or polymer in the reaction solution.

Monodisperse spherical TiO<sub>2</sub> particles with diameters from 200 to 2500 nm were prepared by controlled hydrolysis of titanium tetraethoxide in ethanol. Ethanol was mixed with 0.1 M aqueous salt or polymer solution, and titanium tetraethoxide was added under stirring at ambient temperature. Depending on the concentration, precipitation occurred after a few seconds or minutes and homogeneous TiO<sub>2</sub> beads were formed. After two hours, the reaction was finished and the spheres were filtered and washed with ethanol [2].

Scanning electron micrographs reveal the perfectly uniform spherical shape of the TiO<sub>2</sub> particles (Fig. 1). The size and the size distribution were affected in a rather sensitive way by different salt or polymers which were added to the reaction solution. With alkali halides we observe



**Fig. 1** SEM picture of the titania particles synthesized by addition of Lutensol ON 50.

that the particle size decreases with increasing ionic strength in the reaction solution. Beads with diameters of about 3000 nm were obtained with lithium chloride, whereas the use of cesium chloride yielded 200-nm particles. The electrophoresis results show that an increased positive zeta potential leads to a reduction in particles size. This is correlated with the ionic strength in the reaction medium. Bogush et al. established the growth of the particles is best described by an aggregation mechanism, rather than by the *LaMer* model. The aggregation mechanism implies that the colloidal particles are formed by aggregation of small particles with a size of 5–20 nm (primary particles). The AFM picture of our titania colloids demonstrates that the surface of the final particles is rough: The height variation amounts to about 5 nm. This result indicates that the final particles consist of primary particles with a diameter of about 10 nm.

The influence of polymers on the size and size distribution of the colloidal particles was investigated next. Two different types of polymers, diblock-copolymers Lutensol (RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>H) and triblock-copolymers Pluronic (PEO<sub>n</sub>-PPO<sub>m</sub>-PEO<sub>n</sub>), were used for ster-

ic stabilization, since the polymers can be assumed to stabilize the primary particles in different ways the hydrophilic part of Lutensol is likely to interact with the nanoparticle surface while the hydrophobic part extends into the medium thus providing additional steric stabilization. In case of Pluronic, the presence of two hydrophobic parts can be assumed to lead to a coating of the nanoparticle surfaces. The size of the colloids obtained increases with decreasing length of the hydrophobic part, as expected from the increasing stabilization of the primary particles by a surfactant with long hydrophobic chains. The length of the hydrophilic part, on the other hand, has no effect on the particles size. This part can be assumed to lie closely on the primary particle surface such that it exerts no significant effect on particle stabilization.

The stabilization by Pluronic polymers is not as effective. It results in a broad size distribution of the titania particles. The average size of the particles can be increased with increasing length of the Pluronic polymer.

We assume that the polymer is built into the final particles during the aggregation process. This aggregation model suggests that at the end of the reaction, the particles are porous and the porosity can be controlled by the polymer type. Nitrogen absorption measurements show indeed that the specific surface area ( $a_s$ ), determined by the Brunauer-Emmett-Teller method, increases when the polymer is added to the reaction medium. Lutensol ON 50 yields the largest porosity with  $a_s = 300 \text{ m}^2/\text{g}$ , presumably, because it requires the largest space around the particles and prevents the formation of compact particles. In contrast, the Pluronic polymer stabilizes the primary particles in such a way that the primary particles form more compact aggregates and  $a_s$  decreases to  $200 \text{ m}^2/\text{g}$ . As the electrostatically stabilized colloids are formed without polymer, no porosity is expected and, indeed, the surface area decreases to  $40 \text{ m}^2/\text{g}$ .

X-ray powder diffraction pattern show that the TiO<sub>2</sub> phase thus obtained is amorphous. Thermal analysis, <sup>1</sup>H MAS NMR, and X-ray absorption spectroscopy were carried out to determine the local structure. Thermal analysis clearly demonstrates the release of one water molecule per unit cell, the amorphous phase thus contains water molecules and/or hydroxide ions. The presence of hydroxide was evident from the analysis of <sup>1</sup>H MAS NMR spectra which clearly show three signals. Consequently, the analytical techniques suggest that the idealized chemical compositions of the TiO<sub>2</sub> beads are close to TiO<sub>1.9</sub>(OH)<sub>0.2</sub>·0.9(H<sub>2</sub>O). The XANES spectra of titania compounds show different pre-edge peaks which are ascribed to the 1s–3d transition of the excited electron and contain information about the coordination of the Ti atom. The pre-edge peak of the titania beads obtained without addition of polymer corresponds to very distorted octahedrally coordinated Ti and the pre-edge peak of titania particles obtained by addition of polymer corresponds to octahedrally coordinated Ti. These results indicate that the polymer do not only effect the formation mechanism of the particles but also the structure of the amorphous phase.

- [1] J. H. Jean, T. A. Ring, *Langmuir* **1986**, 2, 251.
- [2] S. Eiden-Assmann, J. Widoniak, G. Maret, *Chem. Mater.* **2004**, 16, 6.
- [3] G. H. Bogush, C. F. Zukoski, *J. Colloid Interface Sci.* **1991**, 142, 1.

DOI: 10.1002/zaac.200470022