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# Influence of additives on size and porosity in the synthesis of uniform TiO₂ Nanoparticles

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**Abstract** Monodisperse spherical titania particles of variable sizes are produced in a sol-gel synthesis from Ti(EtO)$_4$ in ethanol with addition of a salt or a polymer solution. The influence of different salt ions or polymer molecules on the size and on the size distribution of the final particles was investigated. The amorphous hydrous titania particles were characterized by electron microscopy, thermogravimetry, $^1$H-MAS-NMR and X-ray absorption spectroscopy and electrophoresis. Nitrogen absorption measurements revealed that the addition of polymers yields hollow and porous titania colloids.

**Keywords** Titania particles · Size and size distribution · Thermogravimetry · Tailoring particles · Stabilizing polymer

## Introduction

The production of particles of a specific size and morphology is of primary importance for the development of new materials. Mesoscale spheres of ceramic materials are of particular interest for fundamental research, in order to interpret physical properties or surface interactions quantitatively as a function of the morphology and size of the spheres. Recently, the importance of tailored particles has been recognized in a number of applications such as ceramics, catalysts, solar cells [1], pigments and photonic crystals [2]. For optical applications, titania particles are particularly interesting owing to their high refractive index.

Because of their technological importance, different approaches [3–8] have been developed, following the pioneering studies of Matijevic and coworkers [4]. One established method is the precipitation of titania particles from titania alkoxides in aqueous alcohol solution. The method originally reported by Barringer and Bowen [6] was found to be difficult to reproduce and aggregates containing a few spherical colloidal particles were frequently obtained. In previous studies [9, 10], the origins of this morphology were investigated and found to result from an interplay of electrostatic, van der Waals and short-range repulsive interaction potentials. If the particle surface potential is raised to a sufficient level, the repulsive interactions are strong enough to prevent Brownian aggregation and uniform particles are formed. Therefore, one method of controlling the stability of the particles is to increase the charge of the particle surface by adding a salt. In the case of titania, Look and Zukoski [8] added NaCl or HCl to the precipitation medium and obtained particles with diameters between 800 and 1,200 nm, depending on the salt concentration. A second method of controlling the stability of particles is based on the steric stabilization of the particles. Jean and Ring [5] used a polymeric stabilization agent, hydroxypropylcellulose, in order to control the size of the colloids. They obtained particles with diameters in a range between 700 and 1,200 nm. In order to investigate the influence of steric and electrostatic stabilization on the formation mechanism, the size, and the size distribution of titania particles in more detail, we varied the ionic strength and the type of the stabilizing polymer in the reaction solution.

Here, we describe a simple and reproducible synthesis of well-defined hydrous titania particles, which were obtained by adding salt or polymer to the reaction solution. Additionally, we report their characterization

by electron microscopy, thermogravimetry (TG), ^{1}H-MAS-NMR, X-ray diffraction (XRD), nitrogen absorption and electrophoretic mobility measurements and discuss the mechanism of particle formation.

## Experimental

### Synthesis

Monodisperse spherical $TiO_2$ particles were prepared by controlled hydrolysis of titanium tetraethoxide in ethanol [6]. An ethanol volume of 100 ml was mixed with 0.4–0.6 ml of aqueous salt or polymer solution, followed by addition of 1.7–2.0 ml titanium tetraethoxide at ambient temperature under an inert gas atmosphere, using a magnetic stirrer. The reagents must be mixed completely, so that nucleation occurs uniformly throughout the solution. Depending on the concentration, visible particle formation started after several seconds or minutes and gave a uniform suspension of $TiO_2$ beads. After a few minutes stirring was discontinued. After a few hours the reactions were finished and the spheres were collected on a Millipore filter and washed with ethanol.

## Methods of characterization

The water content of the $TiO_2$ beads was determined thermogravimetrically using a Netzsch-thermoanalyzer STA 429 ($O_2$ atmosphere, heating rate 10 K/min) combining TG, differential TG (DTG) and differential thermal analysis (DTA).

The crystallinity and phase-purity of the products was monitored by powder XRD using a Guinier-Huber camera 600 with $CuK''_1$ radiation. Scanning electron micrographs (SEMs) were obtained on a Philips raster electron microscope (XL Series).

Electrophoretic mobility was measured on a Zetasizer (Brookhaven). Particle mobilities were determined by centrifuging particles out of suspension and resuspending a small fraction of particle sediment in the supernatant for use in mobility determinations.

^{1}H MAS NMR spectra of $TiO_2$ particles, dried at 100 °C, were recorded on a Bruker MSL-400 spectrometer at 400.13 MHz resonance frequency with pulse repetition of 120 s, pulse width of 2 $\mu$s and a spinning speed of 10.0 kHz. Nitrogen absorption isotherms were measured at 77 K on a Quantachrome Nova 3000. The samples were outgassed at 475 K and 1 mPa for 12 h.

## Results and discussion
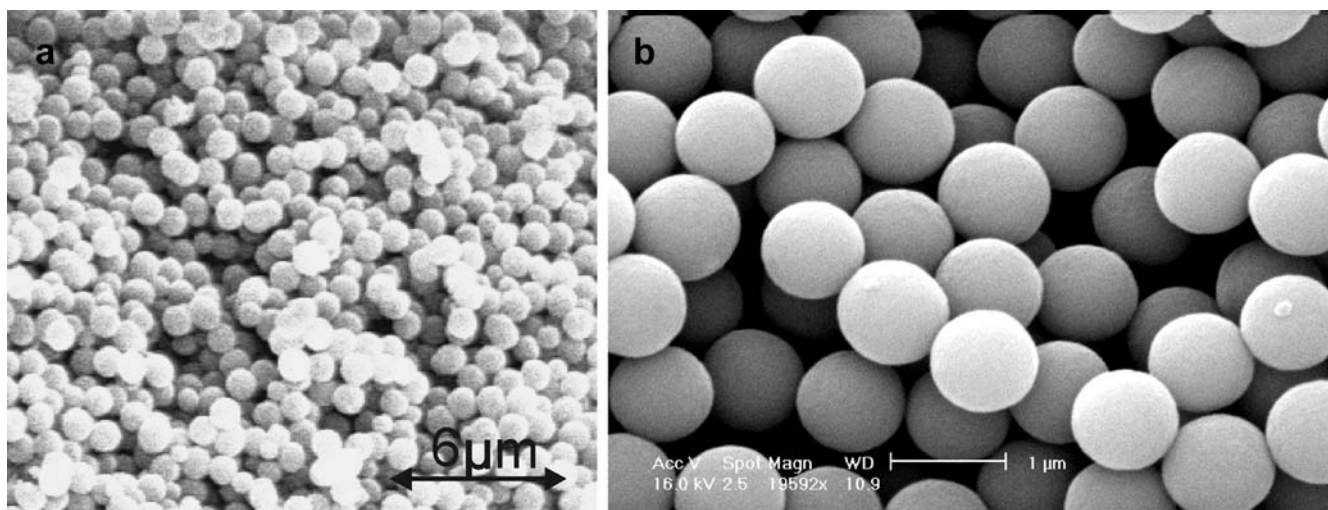
### The addition of salt

The concentration of all reactants were varied, and 100 ml ethanol, 1.70 ml $Ti(OC_2H_5)_4$, and 0.40 ml of 0.1 M aqueous salt or polymer solution were found to be optimal. Variations in the concentration of ethanol,

water or $Ti(OC_2H_5)_4$ showed no significant effect on the size of the particles, but on the size distribution. Moreover, the size and the size distribution are very sensitive to the type of salt that is added (Table 1). SEMs, (cf. Fig. 1a) illustrate that perfectly uniform spherical $TiO_2$ colloids are obtained by addition of salts such as alkali halides and nitrates. With alkali halides we observe that the particle size decreases with increasing ionic strength in the reaction solution. Beads with diameters of about 2,500 nm were obtained with lithium chloride, whereas the use of cesium chloride yielded 200-nm particles. No size changes were obtained when the halide anions were changed; approximately the same results were obtained for alkali bromides and iodides. The electrophoresis results (Table 1) show that an increased positive zetapotential leads to a reduction in particle size. This is correlated, at least for particles formed with KCl, with the ionic strength in the reaction medium. At very high ionic strength no formation of particles was observed. Probably, in this case the ions bind most of the water molecules in the hydration shell, so that not enough water molecules exit for the generation of titania. For different cations, the zetapotential (and hence the degree of cation absorption) increases significantly with increasing cation radii. As judged from EDX measurements, which show no indications of any salt ions, the cations are not built into the particles.

Bogush and Zukoski likewise reported that changes in the ionic strength affect the formation of titania particles. Bogush et al. [11, 12] established that the growth of the particles is best described, rather than by the LaMer model [13], by an aggregation mechanism, which implies that the colloidal particles are formed by aggregation of small particles with a size of 5–20 nm (primary particles). They suggested, furthermore, that the formation of primary particles proceeds independently of the existing particles and that the absolute size of the final particles is determined by the size and the aggregation tendencies of the primary particles.

**Table 1** Size and zeta potential of titania particles depending on the addition of different salt solution under the following conditions: reaction time: 120 min, 100 ml EtOH, 1.70 ml Ti(OEt)₄, 0.40 ml of salt solution

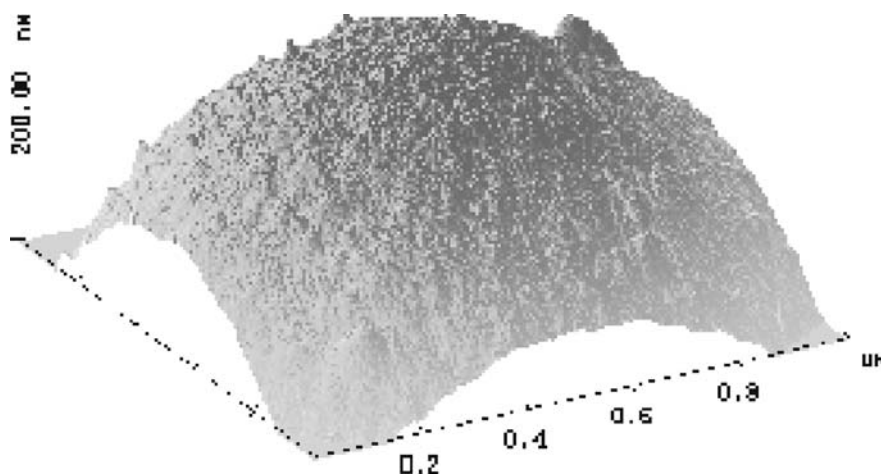|  | Concentration of salt in the reaction solution (M) | Size (nm) | Zeta potential (mV) |
|---|---|---|---|
| LiCl | $4 \times 10^{-4}$ | 700–2500 | 9 |
| NaCl | $4 \times 10^{-4}$ | 800 ± 7% | 16 |
| KCl | $2 \times 10^{-4}$ | 500–900 | 20 |
| KCl | $4 \times 10^{-4}$ | 300 ± 5% | 22 |
| KCl | $8 \times 10^{-4}$ | 50 ± 20% | 27 |
| KCl | $16 \times 10^{-4}$ | No particles | |
| CsCl | $4 \times 10^{-4}$ | 200 ± 20% | 25 |
| KNO₃ | $4 \times 10^{-4}$ | 300 ± 18% | |

**Fig. 1a, b** Scanning electron micrographs (SEMs) of the titania particles synthesized by **a** addition of salt, and **b** addition of Lutensol ON 50

The electrophoresis results show that with increasing stability of the primary particles, the size of the final particles decrease. The effect of the size of the primary particles on the formation of the final particles is difficult to determine. Since the as-synthesized titania particles are amorphous, the size of the primary particles is difficult to determine. The AFM picture shown in Fig. 2 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.

Addition of polymer

The influence of polymers (Table 2) on the size and size distribution of the colloidal particles was investigated next. Two different types of polymers, diblock-copolymers Lutensol [$RO(CH_2CH_2O)_xH$] and triblock-copolymers Pluronic ($PEO_n$-$PPO_m$-$PEO_n$), were used for steric stabilization, since the polymers can be assumed to stabilize the primary particles in different ways (Fig. 3): 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 the case of Pluronic, the presence of two hydrophilic parts can be assumed to lead to a coating of the nanoparticle surfaces. As shown in Fig. 1b, highly monodisperse particles are obtained in the presence of the Lutensol polymer. The size of the colloids obtained increases with decreasing length of the hydrophobic part (Table 2), 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.

**Fig. 2** AFM picture of a titania particle prepared with sodium chloride

**Table 2** Size of titania particles depending on the addition of different polymer solution under following conditions: reaction time: 120 min, 100 ml EtOH, 1.70 ml Ti(OEt)$_4$, 0.40 ml of 0.1 M polymer solution

| Polymer | Formula | Particle size in nm |
|---|---|---|
| Lutensol AO 5 | RO(CH$_2$CH$_2$O)$_5$H R = C$_{13}$C$_{15}$, oxoalcohol | 800 ± 3% |
| Lutensol TO 3 | RO(CH$_2$CH$_2$O)$_3$H R = i–C$_{13}$H$_{27}$, oxoalcohol | 800 ± 3% |
| Lutensol TO 5 | RO(CH$_2$CH$_2$O)$_5$H R = i–C$_{13}$H$_{27}$, oxoalcohol | 800 ± 3% |
| Lutensol TO 7 | RO(CH$_2$CH$_2$O)$_7$H R = i–C$_{13}$H$_{27}$, oxoalcohol | 800 ± 3% |
| Lutensol ON 50 | RO(CH$_2$CH$_2$O)$_5$H R < C$_8$H$_{17}$, fatty alcohol | 1,000 ± 3% |
| Lutensol AN 7 | RO(CH$_2$CH$_2$O)$_7$H R = C$_{12}$C$_{14}$, fatty alcohol | 900 ± 5% |
| Lutensol AT 11 | RO(CH$_2$CH$_2$O)$_{11}$H R = C$_{16}$C$_{18}$, fatty alcohol | 800 ± 5% |
| Pluronic PE 4300 | HO(CH$_2$CH$_2$O)$_x$(CH(CH$_3$)CH$_2$O)$_y$(CH$_2$CHO)$_z$H Molar mass: 1750 g/mol PPO = 30% | 600 ± 20% |
| Pluronic PE 6400 | HO(CH$_2$CH$_2$O)$_x$(CH(CH$_3$)CH$_2$O)$_y$(CH$_2$CHO)$_z$H Molar mass: 2,900 g mol$^{-1}$ PPO = 40% | 600–1300 |



**Fig. 3a, b** Stabilization of primary particles **a** by Lutensol and **b** by Pluronic

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 by increasing the length of the Pluronic polymer.

We assume that the polymer molecules influence the aggregation process by stabilizing the nanoparticles (Fig. 4). 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 (Table 3). Lutensol ON 50 yields the largest porositiy with up to $a_s = 200$ m$^2$ g$^{-1}$, 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 about 100 m$^2$ g$^{-1}$. As the electrostatically stabilized colloids are formed without polymer, no porosity is expected and, indeed, the surface area is smaller than 50 m$^2$ g$^{-1}$.

To compare the influence of various additives on the synthesis of the titania colloids, we measured nitrogen adsorption and desorption isotherms for particles synthesised with 0.1 M solution of Lutensol ON 50, 0.1 M solution of Pluronic PE 6400 and 0.1 M solution of NaCl (Fig. 5). These samples were heated for 12 h at 473 °C for degassing. We can clearly show that the samples prepared with polymer solutions like Lutensol ON 50 (162 m$^2$ g$^{-1}$) and Pluronic PE 6400 (126 m$^2$ g$^{-1}$) possess a higher specific surface area. The volume of adsorbed nitrogen is much higher than in the samples prepared with salts solutions such as NaCl (25 m$^2$ g$^{-1}$).



**Fig. 4** Aggregation mechanism of sterically stabilized primary particles
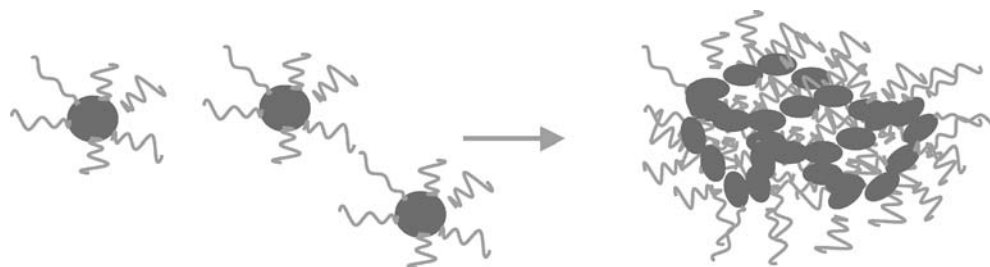
**Table 3** Specific surface area ($a_s$) of titania particles depending on the addition of salt or polymer solution under following conditions: reaction time of 120 min, 100 ml EtOH, 1.70 ml Ti(OEt)$_4$, and 0.40 ml of 0.1 M salt or polymer solution
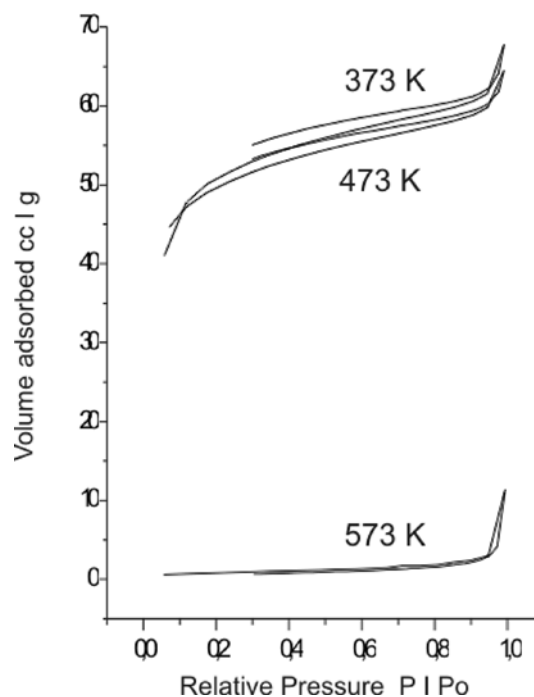
| Salt solution 0.1 M | $a_s$ (m$^2$ g$^{-1}$) |
|---|---|
| NaCl | Up to 50 |
| KNO$_3$ | Up to 50 |
| Lutensol ON 50 | Up to 200 |
| Lutensol ON 50 in vacuum | Circa 100 |
| Pluronic PE 6400 | Circa 100 |
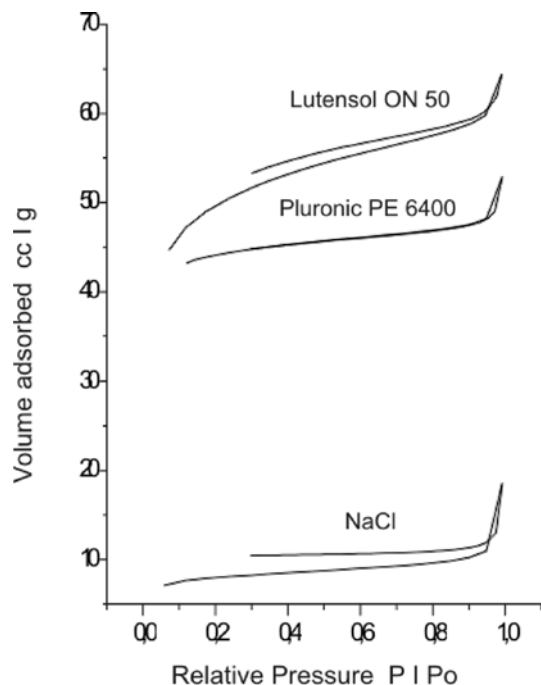


**Fig. 5** N$_2$ adsorption isotherms of titania colloids prepared with a 0.1 M solution of Lutensol ON 50, a 0.1 M solution of Pluronic PE 6400 and a 0.1 M solution of NaCl. The heating conditions are: 12 h at 473 K



**Fig. 6** N$_2$ adsorption isotherms of titania colloids prepared with a 0.1 M solution of Lutensol ON 50. The heating conditions are: 12 h at 373 K, 12 h at 473 K and 12 h at 573 K

The isotherms of titania colloids prepared with 0.1 M solution of Lutensol ON 50 were measured after 12 h degassing at 373 K, 473 K and 573 K (Fig. 6). The specific surface area and, consequently, the pore volumes decreased from 162 m$^2$ g$^{-1}$ for the sample which was heating to 373 K to only 3 m$^2$ g$^{-1}$ for the sample which was heated up to 573 K. Since the size of the colloidal particles did not change, it seems obvious, that the nanoparticles at the surface sintered and closed the passage to the pores inside of colloids. After sintering, nitrogen could no longer fill these pores.

In some cases where hollow or porous titania beads (Fig. 7) were synthezised, the porosity could be observed by SEM. To determine whether all colloid particles were hollow, they were heated up to 1,000 °C. At this temperature, the particles broke down to nanoparticles, which is the expected behavior for hollow titania beads [14]. As no carbon was found in the samples with EDX or elemental analysis, and since the pores are much larger than the micelles formed by these polymers [15], we believe that the cause for the formation of these hollow particles is not only the polymer, but tiny air bubbles that are stabilized by the polymer. When the pressure above the solution was reduced, air bubbles could be observed by eye and less porous and smaller particles were formed. The air bubbles, together with the polymer, might act as seeds on which the titania nanoparticles grow into either hollow beads or porous particles [16]. Similar conclusions were reached by J. Rudloff et al. [19, 20] for the crystallization of CaCO$_3$ in the presence of CO$_2$ bubbles and polymer. A detailed more study of this aspect of the formation process is in progress.

Structure determination

Powder XRD patterns showed that the TiO$_2$ phase thus obtained is amorphous. Thermal analysis, $^1$H MAS NMR, and X-ray absorption spectroscopy were carried out to determine the local structure. Thermal analysis (Fig. 8) clearly demonstrates the release of one water molecule per unit cell; the amorphous phase thus contains water molecules and/or hydroxide ions. DTA
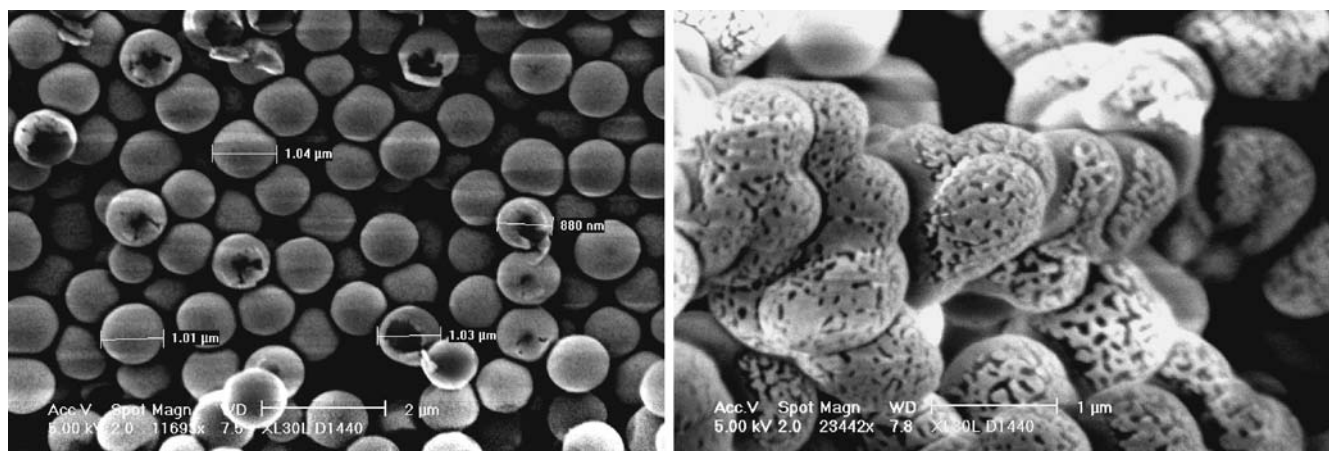
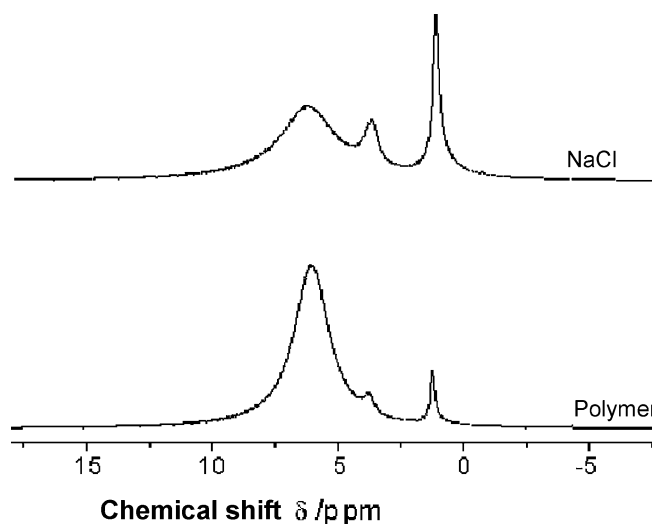

**Fig. 7** SEM pictures of hollow titania particles produced by addition of Pluronic PE 6400 and porous titania particles produced by addition of Lutensol ON 50
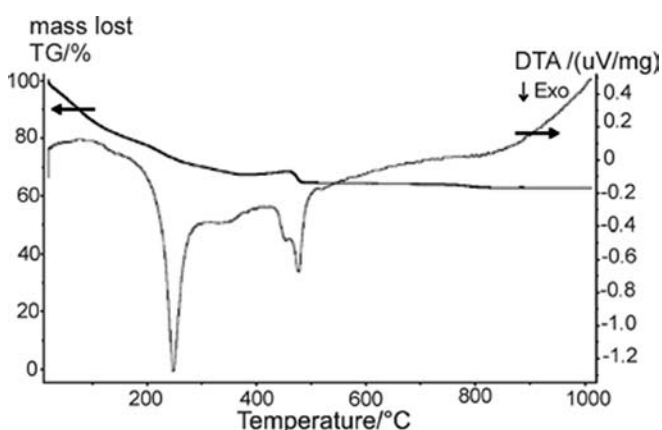


**Fig. 8** Thermoanalysis of the amorphous titania beads. *TG* Thermogravimetry, *DTA* differential thermal analysis



**Fig. 9** 1H MAS NMR measurements of titania particles obtained by addition of salt and by polymer

measurements show three peaks, the first one at about 250 °C and the second one at 450 °C correspond to the release of water, while the third one at 480 °C indicates a phase transition to anatase. For the phase transition to rutile no DTA peak can be observed, since this phase transition runs from 600 to 1,000 °C. The presence of hydroxide was evident from the analysis of $^1$H MAS NMR spectra (Fig. 9), which clearly show three signals: The line at 1.3 ppm corresponds to hydrogen atoms of terminal Ti-OH and the signals at 3.8 and 6.1 ppm to differently bonded water species. Consequently, the analytical techniques suggest that the idealized chemical compositions of the $TiO_2$ beads are close to $TiO_{1.8}(OH)_{0.4} \cdot 0.8(H_2O)$ when formed in the presence of salt and to $TiO_{1.9}(OH)_{0.2} \cdot 0.9(H_2O)$ by the addition of polymer. These results show that more hydroxide groups are associated with the electrostatic stabilization than with steric stabilization.

## Conclusion

We have shown that size, porosity and monodispersity of colloidal titania particles can be controlled by careful choice of surfactants and of salts added during the synthesis. We obtained particles with a narrow size distribution from 50 nm to 2,500 nm in diameter and of variable porosity. In particular, we have synthesized very monodisperse titania particles with diameters of 800 and 1,000 nm in a reproducible way by using the diblock-copolymer Lutensol. This opens up the possibility of using titania particles in photonic applications.

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