Articles

Synthesis and Characterization of Porous and Nonporous Monodisperse Colloidal TiO_2 Particles

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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 the size distribution of the final particles was investigated. The amorphous hydrous titania particles were characterized by electron microscopy, thermogravimetry, ^{1}H-MAS NMR, X-ray absorption spectroscopy, and electrophoresis. Nitrogen absorption measurements revealed that the addition of polymers yields hollow and porous titania colloids.

Introduction

The production of particles with 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 due to their high refractive index.

Because of the technological importance of titania particles, different approaches[3−8] to their synthesis have been developed, following the pioneering studies of Matijevic and co-workers.[4] One established method is the precipitation of titania particles from titania alkoxides in aqueous alcohol solution. This method, originally reported by Barringer and Browen,[6] was found 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 1200 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, to control the size of the colloids. They obtained particles with diameters in a range between 700 and 1200 nm. 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. We also report their characterization by electron microscopy, thermogravimetry, ^{1}H-MAS NMR, X-ray absorption spectroscopy, nitrogen absorption, and electrophoretic mobility measurements and discuss the mechanism of particle formation.

Experimental Section

Synthesis. Monodisperse spherical TiO_2 particles were prepared by controlled hydrolysis of titianium tetraethoxide

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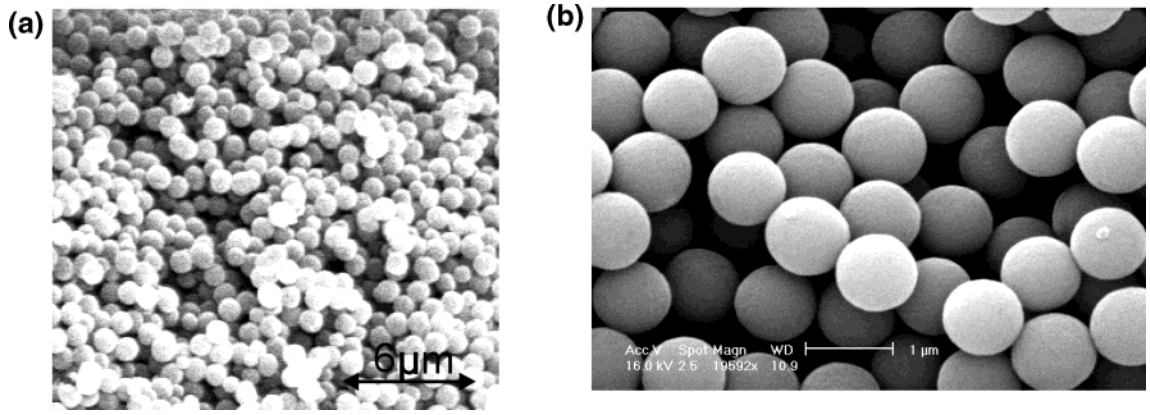

Figure 1. SEM pictures of the titania particles synthesized by (a) addition of salt and (b) addition of Lutensol ON 50.

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 of titanium tetraethoxide at ambient temperature under inert gas atmosphere, using a magnetic stirrer. Reagents had to be mixed completely so that nucleation would occur 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 thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA).

The crystallinity and phase-purity of the products was monitored by powder X-ray diffraction (XRD) using a Guinier-Huber camera 600 with Cu $K\alpha_1$ radiation. Scanning electron micrographs (SEM) 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.

^1H 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 μs, 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.

X-ray absorption spectroscopic measurements of titania colloids were carried out at station E4 of HASYLAB (DESY, Hamburg, Germany). The Ti K-edge EXAFS spectra were obtained in transmission mode under the ring operation conditions of 1.998 GeV and 140−230 mA. The data were analyzed with the program WinXAS 2.2, developed by Ressler.

Results and Discussion

Addition of Salt. The concentrations of all reactants were varied. Optimal conditions were found to be 100 mL of ethanol, 1.70 mL $Ti(OC_2H_5)_4$, and 0.40 mL of 0.1 M aqueous salt or polymer solution. Variations in the concentration of ethanol, water, or $Ti(OC_2H_5)_4$ showed no significant effect on the size of the particles, but did influence the size distribution. Moreover, the size and the size distribution are very sensitive to the type of salt that is added (Table 1). Scanning electron micrographs (Figure 1a) illustrate that perfectly uniform spherical TiO_2 colloids are obtained by addition of salts

Table 1. Size and Zeta Potential of Titania Particles Depending on the Addition of Different Salt Solutions[a]

	salt concentration in reaction solution (M)	size (nm)	zeta potential (mV)
LiCl	$4\cdot10^{-4}$	700−2500	9
NaCl	$4\cdot10^{-4}$	800 ± 7%	16
KCl	$2\cdot10^{-4}$	500−900	20
KCl	$4\cdot10^{-4}$	300 ± 5%	22
KCl	$8\cdot10^{-4}$	50 ± 20%	27
KCl	$16\cdot10^{-4}$	no particles	
CsCl	$4\cdot10^{-4}$	200 ± 20%	25
KNO_3	$4\cdot10^{-4}$	300 ± 18%	

[a] Conditions: reaction time 120 min, 100 mL of EtOH, 1.70 mL of $Ti(OEt)_4$, and 0.40 mL of salt solution.

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 2500 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 with particles formed with KCl, with the ionic strength in the reaction medium. With 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 exist 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

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Table 2. Size of Titania Particles Depending on the Addition of Different Polymer Solutions[a]

polymer	formula	particle size (nm)
Lutensol AO 5	$RO(CH_2CH_2O)_5H$ $R = C_{13}C_{15}$, oxo alcohol	800 ± 3%
Lutensol TO 3	$RO(CH_2CH_2O)_3H$ $R = i - C_{13}H_{27}$, oxo alcohol	800 ± 3%
Lutensol TO 5	$RO(CH_2CH_2O)_5H$ $R = i - C_{13}H_{27}$, oxo alcohol	800 ± 3%
Lutensol TO 7	$RO(CH_2CH_2O)_7H$ $R = i - C_{13}H_{27}$, oxo alcohol	800 ± 3%
Lutensol ON 50	$RO(CH_2CH_2O)_5H$ $R < C_8H_{17}$, fatty alcohol	1000 ± 3%
Lutensol AN 7	$RO(CH_2CH_2O)_7H$ $R = C_{12}C_{14}$, fatty alcohol	900 ± 5%
Lutensol AT 11	$RO(CH_2CH_2O)_{11}H$ $R = C_{16}C_{18}$, fatty alcohol	800 ±5%
Pluronic PE 4300	$HO(CH_2CH_2O)_x(CH(CH_3)CH_2O)_y(CH_2CHO)_zH$ molar mass: 1750 g/mol PPO = 30%	600 ± 20%
Pluronic PE 6400	$HO(CH_2CH_2O)_x(CH(CH_3)CH_2O)_y(CH_2CHO)_zH$ molar mass: 2900 g/mol PPO = 40%	600−1300

[a] Conditions: reaction time 120 min, 100 mL of EtOH, 1.70 mL of $Ti(OEt)_4$, and 0.40 mL of 0.1 M polymer solution.

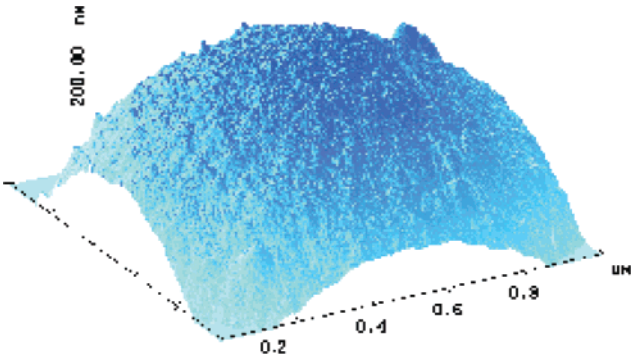

Figure 2. AFM picture of a titania particle prepared with sodium chloride.

(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.

The electrophoresis results show that with increasing stability of the primary particles the size of the final particles decreases. The effect of the size of the primary particles on the formation of the final particles is difficult to determine. Because the as-synthesized titania particles are amorphous, the size of the primary particles is difficult to determine. The AFM picture shown in Figure 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, as the polymers can be assumed to stabilize the primary particles in different ways (Figure 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 case of

Figure 3. Stabilization of primary particles by (a) Lutensol and (b) Pluronic.

Pluronic, the presence of two hydrophilic parts can be assumed to lead to a coating of the nanoparticle surfaces. As shown in Figure 1b, highly monodisperse particles are obtained in the presence of 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 particle 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.

To determine whether the polymer is built into the colloidal particles during the aggregation process, we carried out EDX measurements and X-ray powder diffraction. EDX measurements of the colloidal particles show that these particles contain around 7% carbon which stems from the polymer. This result was corroborated by X-ray diffraction experiments with both electrostatically and sterically stabilized colloids heated to 400 °C (anatase phase). Two typical diffraction patterns are shown in Figure 4. In the case of electrostatic stabilization the width of the Bragg peaks is narrow, corresponding to larger nanoparticles, and in the case of steric stabilization the width is broad, corresponding to very small nanoparticles. This indi-

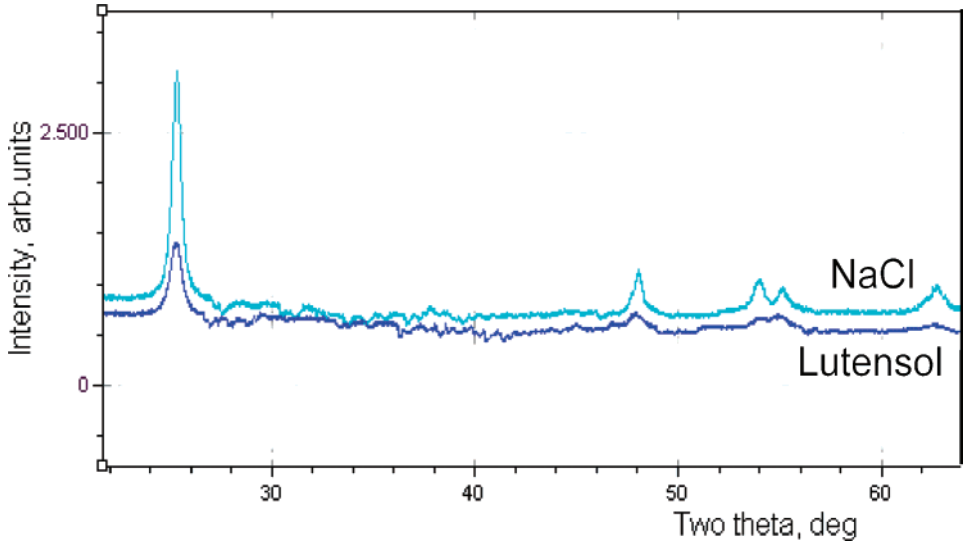

Figure 4. X-ray powder diffraction patterns of anatase colloidal particles which were obtained by steric and electrostatic stabilization.

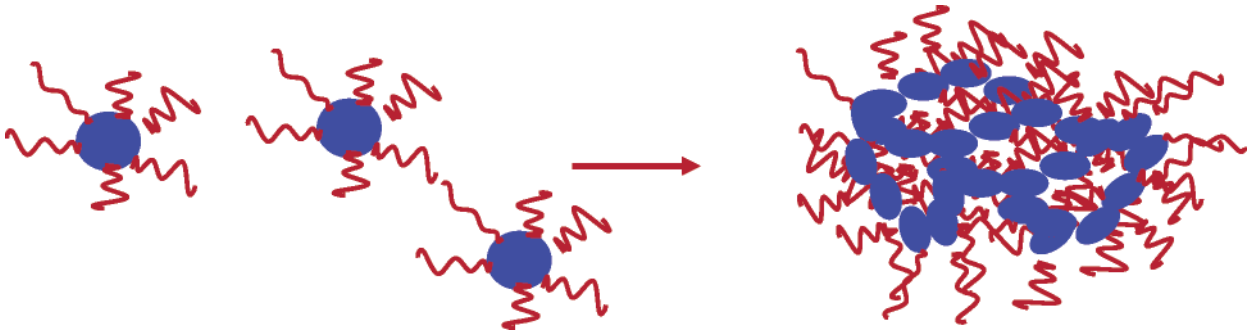

Figure 5. Aggregation mechanism of sterically stabilized primary particles.

Table 3. Specific Surface Area of Titania Particles Depending on the Addition of Salt or Polymer Solution[a]

salt solution (0.1 M)	specific surface area (m^2/g)
NaCl	95
KNO_3	35
Lutensol ON 50	300
Lutensol ON 50 in a vacuum	130
Pluronic PE 6400	200

[a] Conditions: reaction time 120 min, 100 mL of EtOH, 1.70 mL of $Ti(OEt)_4$, 0.40 mL of 0.1 M salt or polymer solution.

cates that electrostatically stabilized nanoparticles can grow together during the sintering process and that in the case of steric stabilization the polymer around the primary particles prevents the formation of larger particles. Therefore, we assume that the polymer is built into the final particles during the aggregation process (Figure 5). 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 porosity with a_s = 300 m^2/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 m^2/g. As the electrostatically stabilized colloids are formed without polymer, no porosity is expected, and, indeed, the surface area decreases to 35 m^2/g.

In some cases where hollow or porous titania beads (Figure 6) were synthesized the porosity can be observed by SEM. To determine whether all colloid particles are hollow, they were heated to 1000 °C. At this temperature, the particles broke 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 because 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 Rudloff et al.[19,20] for the

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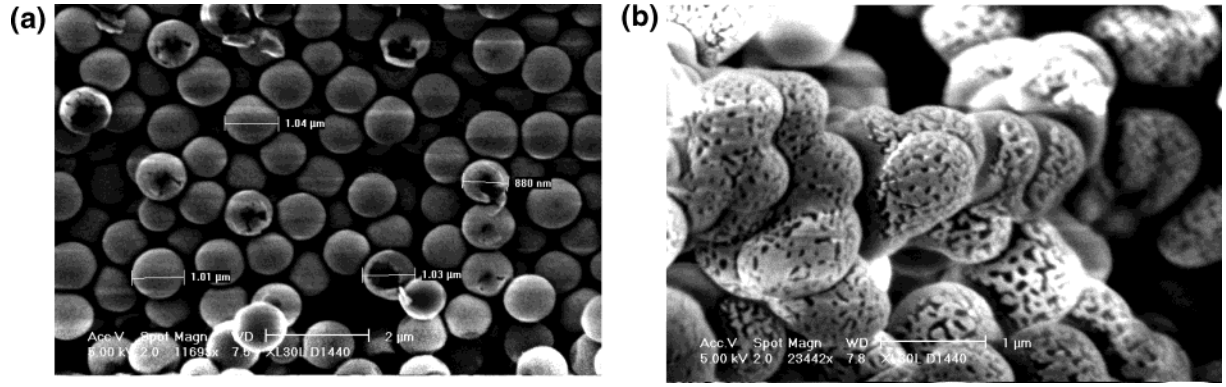

Figure 6. SEM pictures of (a) hollow titania particles produced by addition of Pluronic PE 6400 and (b) porous titania particles produced by addition of Lutensol ON 50.

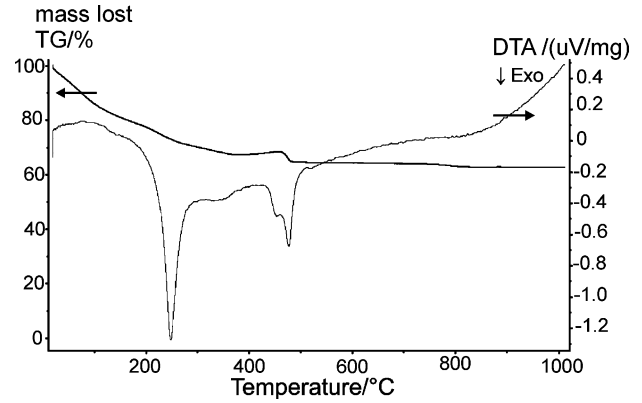

Figure 7. Thermoanalysis of the amorphous titania beads.

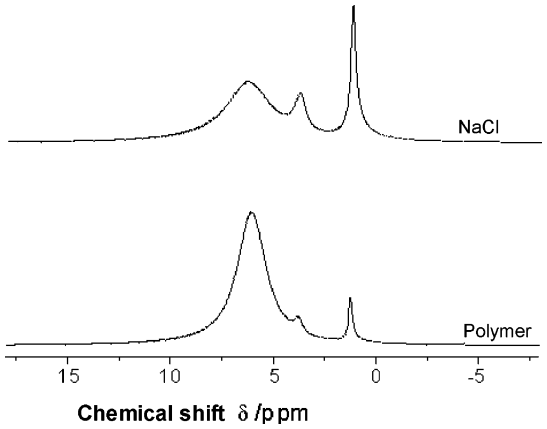

Figure 8. ^{1}H MAS NMR measurements of titania paticles obtained by addition of salt and by polymer.

crystallization of $CaCO_3$ in the presence of CO_2 bubbles and polymer. A more detailed study of this aspect of the formation process is in progress.

Structure Determination. X-ray powder diffraction patterns show 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 (Figure 7) clearly demonstrates the release of one water molecule per unit cell, the amorphous phase thus contains water molecules and/or hydroxide ions. DTA 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, because this phase transition runs from 600 to 1000 °C. The presence of hydroxide was evident from the analysis of ^{1}H MAS NMR spectra (Figure 8) 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 correspond 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 close 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. To investigate the amorphous structure of the hydrous titania phase, X-ray absorption near edge spectroscopy (XANES) was carried out. The spectra (Figure 9) 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.[17] Compounds with tetrahedrally coordinated Ti show strong absorption. Octahedral coordination results in less pronounced features, and up to three peaks may be observed. With increasing distortion, the central peak

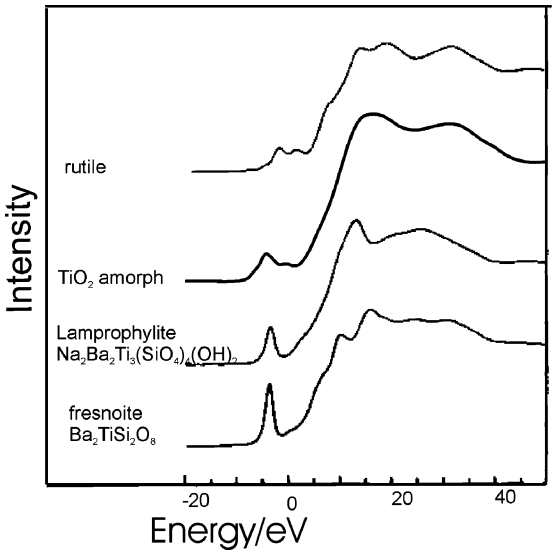

Figure 9. Normalized Ti K-XANES spectra of the amorphous titania particles and three reference compounds: rutile, lamprophylite, and fresnoite.

(20) Rudloff, J.; Ph.D. Thesis, University of Potsdam, Germany, 2001.

gains intensity. The pre-edge peak of the titania beads corresponds to very distorted octahedrally coordinated Ti. The plot of the Fourier transformed EXAFS function shows only one high peak corresponding to a Ti−O distance; the second peak corresponding to a Ti−Ti distance is very small. This indicates that the amorphous structure is highly disordered. Because the compound is unordered and contains water, it is similar to a gel. Imhof[18] reported that his hollow titania particles were deformed after removal of the polystyrene beads on which they had been grown. This indicates that the structure is very flexible.

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 narrow size distribution from 50 to 2500 nm in diameter of variable porosity. In particular, we have synthesized very monodisperse titania particles with diameters of 800 and 1000 nm in a reproducible way by using the diblock-copolymer Lutensol. This opens up the possibility to use titania particles in photonic applications.

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