Abstract
Titanium dioxide has photocatalytic properties, i.e. under UV irradiation it develops an oxidative potential. In photocatalysis this is very desirable, but not when nano particulate titania is embedded into organic polymer matrices in order to increase the refractive index. UV irradiation would in this case destroy the material in the long run. For deactivation in general the titania is coated by e.g. silica or alumina which leads to other undesired effects like growth of the particle size and enhanced light scattering. The current work focuses on the application of techniques for doping during synthesis or crystallization of nano particulate TiO$_2$. The photocatalytic activity was determined by degradation experiments of 4-chlorophenol using dip coated glass plates under artificial sunlight, where decreases of the photocatalytic effect of up to 90% were found.

Background
In order to increase the refractive index of a composite material, it is often necessary to embed high refractive index oxides into organic polymeric matrices. For optical applications – like reflective or anti reflective coatings – the use of highly transparent composite materials is a must. Therefore light scattering has to be avoided. For that reason the particle size of the embedded material needs to be smaller than about 1/20 of the shortest wavelength under use. With 400 nm as the low wavelength limit for the human vision, this translates to a size limit of 20 nm that may not be surpassed for the application fields.

Titania, both in the anatase as well as in the rutile modification, has a sufficiently high refractive index for the previously described application. Furthermore there are established preparation techniques [1] to obtain nano particles of anatase with mean particle sizes of 10 nm or less. These can be re-dispersed in suitable solvents or matrices at the level of the primary particles without any significant aggregation or agglomeration. However anatase shows a very high photocatalytic potential. This means that under UV irradiation, it develops a significant oxidative property. This can be explained by a look at the band structure of the semiconductor titania. The gap between the edges of the conductive (CB) and the valence band (VB) is 3.05 eV in the case of rutile and 3.23 eV in the case of anatase. This means that UV-photons can promote an electron from the VB to the CB. There are two reaction systems starting from water and oxygen respectively which can be initiated by the promoted electron or the hole remaining in the VB after the promotion. They lead to the formation of hydroxyl radicals being responsible for the oxidative attack on organics.

Although photocatalysis is desirable in many applications, it leads to problems when the material is embedded in organic matrices, where the UV irradiation leads to several undesired effects starting from yellowing of the matrix material and
The ongoing work is targeted on the application of doping techniques using sodium ions to nanoscaled titania during the synthesis or crystallisation phase. Variations of the concentration of the dopant material and studies of the crystallization under lyothermal conditions were performed. This variation was necessary in order to minimize the deteriorating effects, especially a tendency towards particle growth.

Experimental

Preparation of the titania nanoparticles

The titania particles were prepared by a precipitation-crystallization technique starting from organic titania precursors such as titanium tetraisopropylate, Ti(OiPr)₄. These precursors were diluted in suitable solvents, and were mixed with – soluable or partially soluable – sodium compounds (see below in chapter results) either before, during, or after the hydrolyzation step. For this, the mixture was treated with acids such as hydrochloric acid and a stoichiometric or sub-stoichiometric amount of water. This treatment was executed in such a manner, that in no point of time large, visible precipitates of gel or flocculates were formed in the sol. If such coarse-particles were formed, it was impossible to obtain nano particulate titania as the final product.

The sol was treated in a lyothermal process in order to obtain crystalline titania particles of anatase. Therefore, the sol was transferred into stainless steel pressure vessels with Teflon liners, and was treated destruction of the synthesized material in the long term.

Rutile compared to anatase has a significantly lower photocatalytic activity, but being the high temperature modification, the formation of rutile from amorphous or anatase material in general leads to much bigger primary particles which are not suitable for the incorporation into transparent polymers for optical applications.

To elude the photocatalytic activity, methods are described in literature which are mainly based on covering the titania with shells of inert, isolating layers such as silica or alumina [2]. In general, this procedure leads to an increased particle size and thus to increased scattering of light. This is good for pigment applications, but not suitable for the described optical composite materials mentioned before.

Certain metals are known to “poison” the photocatalytic effect, by forming recombination sites in the titania, where exciton pairs are annihilated, preventing the oxidative effects. Attempts have been described utilizing the doping of the titania with ions of manganese or chromium [3]. The incorporation of these ions leads to a change in the band structure of the titania and a reduction of the band gap. The before mentioned reaction systems can no longer be activated diminishing the activity. But due to the reduction of the band gap, also blue light is absorbed by such a material, leading to a strong yellowing effect in comparison to undoped titania.
at temperatures between 150 and 250 °C under autogenously formed pressure. After a successful treatment, the vessels contained two phases, an organic liquid which was almost void of titanium and a precipitate in the form of a white slurry. This white slurry could be dried under reduced pressure and gave a white paste or powder, which was readily dispersible in deionized water or diluted acids, e.g. hydrochloric acid with c=1 mole/l. When dispersed in deionized water, the acidity of the dispersion obtained was around pH 2-3.

Preparation of thin films
For the evaluation of the photocatalytic behaviour of the materials, thin films on glass substrates were produced. A clear TiO₂ sol was used for this application. 1 g of nanoparticles were dispersed together with 1 g of 3,6,9-Trioxa-decanoic acid (TODA) in 19 g of an ethanol / water mixture of 50:50 by weight. For the application of the thin film a dip coating apparatus was utilized. The films were drawn at a speed of 2 mm/s and dried at 200 °C.

Photocatalytic degradation experiments
Photo degradation experiments were performed for the evaluation of the photocatalytic activity of the doped TiO₂ nanoparticles. 4-Chlorophenole (4-CP) was used as the model substance. Sample solutions with a concentration of 4-CP of c = 50 µmoles/l were prepared. For each experiment a microscope slide was used; the coated surface of the slide was 9.25 cm², the volume of the 4-CP solution used in each experiment was 50 mL. The degradation experiments were performed under artificial solar light using an Atlas Sun tester CPS+ equipped with a 750 W Xenon lamp. The concentration of the 4-CP was determined by UV-Vis spectroscopy. As a reference, films prepared with undoped anatase obtained from INM’s standard process [4] were used.

Results
The effect of deactivation of titania by utilizing sodium dopant was reached fast, but the optimisation towards particles with suitable sizes took significant experimental work.

This work originally started with the idea of using sodium metholate as the hydrolysis catalyst for the formation of titaniumoxide / titaniumhydroxide from titanialcoholate precursors. When mixtures of Na-methanolate with an alcohol used as a dilutor were combined with titani- umalcoholates, only very big amorphous particles were obtained, delivering milky white suspensions. As so often, hydrolysis with strong bases leads to a fast particle growth.

When mixtures of Na-methanolate with an alcohol were adjusted with hydrochloric acid to acidic conditions, most of the sodium was removed from the mixture by the precipitation of sodiumchloride crystals. Under these conditions, as well
TEM pictures also NaCl-crystals were found, it was tested whether thin films prepared from mixtures of photocatalytically active anatase with sodium chloride showed a reduction of the photocatalytic activity: the results were negative.

Smaller particles with significantly reduced photocatalytic activity were only prepared upon changing the dopant to sodium carboxylates such as sodium acetate or sodium oleate. In first experiments particles with sizes of 20 to 50 nm were obtained, a significant improvement compared to the first attempts but still much to large for transparent composite materials. Additional work resulted in samples of Na-doped anatase with small particle sizes (< 12 nm) and strongly diminished photocatalytic properties. In Figure 1, a transmission electron micrograph (TEM) of a sample of Titania doped with 2 wt% sodium is shown. Figure 2 depicts two samples of dispersions of sodium doped titania with 1 and 2 atom % sodium, respectively. In order to prepare these 10 wt% aqueous dispersions, no additional detergent or dispersing agent was needed. In Figure 3, the XRD data from a particle sample doped with 1 atom % sodium is plotted. The material obtained has anatase crystal structure with a mean crystallite size of 6 nm. Furthermore additional signals from halite were found; these sodium chloride crystals are due to the sample preparation, as no cleaning steps of the particles were executed. As in some of the TEM pictures also NaCl-crystals were found, it was tested whether thin films prepared from mixtures of photocatalytically active anatase with sodium chloride showed a reduction of the photocatalytic activity: the results were negative.

Figure 4 shows a typical degradation experiment with two sample films drawn from dispersions doped with 1 and 2 atom % Na in comparison to an undoped material. It can be seen, that in the 60 hours experiment with the undoped material, the test substance 4-CP was completely degraded, whereas in the 60 hours experiments involving the doped materials about 85 % of the 4-CP still remained unchanged after this time.

Figure 3: XRD Data from titania doped with 1 atom % sodium. Depicted are the measured signal as well as the signal positions of anatase and halite.

Figure 4: Degradation experiment applying films coated with Na-doped titania in comparison with undoped titania obtained from INM standard procedure.
Outlook

By further optimization of the doping process, e.g. by variations of doping timing or precursor substance, it is intended to further decrease the photocatalytic properties as well as to enhance the particulate properties like particle size.

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References