Doped nanoparticles for photocatalytically active surfaces

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For the fabrication of transparent coatings, various routes have been investigated. Doped and undoped TiO_2 nanoparticles have been prepared by hydrothermal and reflux synthesises. Fully crystallized systems down to 4-5 nm, fully redispersible in organic solvents as well as in water have been obtained. The doped systems show significantly higher activities in the decomposition of organic dyes, and the band edge could be shifted to the visible range. These particles have been additionally surface modified to be able to disperse them in the matrix of the coating material. Single and double layer coatings with self-cleaning and hydrophilic properties have been prepared using the described particles.

Key words: nanoparticles, wet coating, surfaces

1. INTRODUCTION

The photocatalytic property of TiO_2 is known since a long time [1-5]. The effect is due to an electron-hole pair formation if, for example, in anatase UV-light with a wave-length less than 388 nm hits TiO_2 particles. Due to the diffusion of the hole and of an electron (with the subsequent formation of peroxides from water and oxygen from the atmosphere) to the surface, an oxidation potential of 3.2 electron volts is obtained. This has been used for the preparation of photocatalytically active surfaces as shown by Fujishima, Watanabe and Hashimoto [6, 7, 8]. Many attempts have been made to dope TiO_2 with elements like Al^{3+} (one excess electron) or P^{5+} (one electron lacking) in order either to enhance the photocatalytic activity or to shift the absorption to longer wave lengths (visible light photocatalysis). As pointed out by Herrmann [9] clearly, it was not possible to improve the photocatalytic activity by lattice doping, showing that in all cases the efficiency was reduced mainly based on the fact that the recombination time is reduced. As shown by Watanabe [10], the deposition of TiO_2 on WO_3 transparent thin films on glass, the potential of which was kept at zero by connecting it to the ground, an enhancement of the photocatalytic activity, for example, in form of an improved hydrophilicity could be shown. This can be interpreted by the hypothesis that the recombination time can be increased by offering the electron an extra space. For this reason, it has been investigated whether the combination of anatase nano particles with semi-conducting oxide particles may have a similar effect. For this reason, TiO_2 nanoparticles have been synthesized for the combination with WO_3 and $Cr(III)$, in order prepare for coatings from these composite particles. For reasons of easy coating techniques, the gradient formation using nanoparticles also was investigated together with NANOMER® matrix systems.

2. EXPERIMENTAL

2.1 Fabrication of anatase nanoparticles by a lyothermal process

In a round bottom flask 145.1 g 1-propanol were mixed with 96 g titanium tetraisopropylate under heavy stirring. After 2 min mixing time 6.66 g of a 37 wt.-% hydrochloric acid were added dropwise while continuing the agitation. After another 20 min, 7.12 g water were added in a similar way. The solution was stirred for another 10 min, after which the obtained sol was diluted with 419.67 g 1-propanol. The obtained sol is stable for some months and is referred to as pre-titania sol. 160 ml of the pre-titania sol were measured into a 250 ml Teflon vessel, which was placed in a stainless steel pressure vessel. The pressure vessel was transferred into a metal heating block in order to be autoclaved at 250 °C with a temperature ramp of 50 min for the heating from room temperature to 250°C followed by additional 6 hours of hold time. The autoclave vessel was allowed to cool down at room temperature in the heating block. The procedure was executed over night, so the next morning temperatures below 50 °C were reached and the pressure vessel could be opened. The reaction mixture was centrifuged (Megafuge 2.0 R by Heraeus , 500 ml PP-centrifugation vessels at 4000 rpm for 30 min). The liquid phase was disposed. The solid paste was transferred into a round bottom flask and dried using a rotary evaporator at 40 °C bath temperature and reduced pressure. Further drying could be executed in an evacuated drying chamber over night at 40 °C. Around 15 g of a slightly yellowish powder were obtained per 160 ml set-up of sol. The powder was completely redispersable in toluene up to aruond 20 wt.-% of nano titania.

2.2 Fabrication of anatase nanoparticles by the reflux route

A heating bath was preheated to 135 °C before starting the procedure described below. 162.45 g 1-pentanol were mixed at room temperature with 107.51 g titanium tetraisopropylate in a round-bottomed flask under heavy stirring. After 2 min mixing time 7.458 g of a 37 wt.-% hydrochloric acid were added drop wise while continuing the agitation. After another 10 min, 7.973 g water were added in a similar way. During the addition of the water, the solution was getting opaque. When larger particles or a white precipitate was observed, the continuation of the process did not yield redispersible nanoparticles. The solution was stirred for another 20 min and the flask afterwards was transferred into the heating bath.

The mixture was held at boiling temperature under reflux for 16 hours. The reaction mixture was centrifuged (Megafuge 2.0 R by Heraeus, 500 ml PP-centrifugation vessels at 4000 rpm for 30 min). The liquid phase was disposed. The solid paste was transferred into a round-bottomed flask and dried using a rotary evaporator at 40 °C bath temperature and reduced pressure. Further drying could be executed in an evacuated drying chamber over night at 40 °C. Around 14 g of a slightly yellowish powder were obtained. The powder was completely redispersable in 0.01 N hydrochloric acid up to around 10 wt.-% of nano titania. The particle size distribution was determined by photon correlation spectroscopy and TEM analysis.

2.3 Surface modification of the anatase nanoparticles from the lyothermal process

1.002 g of the dry nano titania particles obtained from the lyothermal process were stirred in 9.040 g of dry toluene and a solution of 0.268 g stearic acid in 5.015 g dry toluene was added. By ultra sonic agitation for at least 15 min a sol was obtained. The sol was centrifuged at 8000 rpm in 45 ml PP centrifuge vessels (Dow-Corning) using a Hermle Z323K centrifuge in order to remove agglomerates. The solids were discarded and the sol was transferred in round-bottomed flask, mixed with 0,146 g 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-1,1,1-triethoxysilane (FTS) and stirred in the dark for 16 hours. Afterwards the solvents were evaporated using a rotary evaporator at 40 °C bath temperature and reduced pressure to obtain a dry powder. Further drying could be executed in an evacuated drying chamber over night at 40 °C.

2.4 Surface modification of the anatase nanoparticles from the reflux process

1.007 g of the dry titania particles obtained from the reflux process were dispersed in 9.075 g of dry toluene by ultra sonic agitation for 15 min. This sol was centrifuged at 8000 rpm in 45 ml PP centrifuge vessels (Dow-Corning) using a Hermle Z323K centrifuge in order to remove agglomerates. The solids were discarded and the sol was transferred in round bottom flask, mixed with 0.234 g 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-1,1,1-triethoxysilane (FTS) and stirred in the dark for 16 hours. Afterwards the solvents were evaporated using a rotary evaporator at 40 °C bath temperature and reduced pressure to obtain a dry powder. Further drying could be executed in an evacuated drying chamber over night at 40 °C.

2.5 Doping with tungsten (VI) oxide (1 atom-% of W)

155 ml of the pre-titania sol from step 2.1 were measured into a 250 ml Teflon vessel. 0.135 g of a tungsten(VI) oxide (Merck) were added. Afterwards the sol was agitated in an ultrasonic bath for 5 min. Then the vessel was transferred in a stainless steel pressure container and treated as described in step 2.1.

2.6 Doping with chromium(III) acetyl acetonate (1 atom-% of Cr)

Chromium doped particles were obtained by both routes. For the lyothermal route 155 ml of the titania pre-sol from step 2.1 were measured into a 250 ml Tef-

lon container. 0.228 g chromium(III) acetyl acetonate (Merck 802485) were added. Afterwards the sol was agitated in an ultra sonic bath for 5 min. Then the vessel was transferred into a stainless steel pressure vessel and treated as described in step 2.1.

For the reflux route, 10 min after the addition of the water as described in step 2.2, 1.33 g chromium(III) acetyl acetonate (Merck 802485) were added and the solution was stirred for another 10 min. Then the sol was brought to a boil and the procedure as described in step 2.2 was continued.

2.7 Fabrication of the self-aligning gradient coatings

As a experimental matrix system a epoxysilane hydrolysate was used. 5.4 g of distilled water were added slowly to 23.6 g of GLYMO (3-glycidyloxypropyl trimethoxysilane) and the mixture was stirred over night. 50 mg nano-TiO2 modified with FTS were dispersed in 1.56 g methylethylketone (MEK) by ultrasonic treatment and 0.44 g of formamide were added. Under stirrring 1.034 g of the GLYMO hydrolysate were mixed with sol of modified nano-TiO2 in MEK and the formamide.

The application of the coatings was done on glass, plastics (e.g. PC) or metal by dip-coating, spin-coating or flow-coating. The wet film was allowed to pre-dry at room temperature before the coated substrates were transferred into an oven for at least 1 h at 130 °C. Longer curing times or higher curing temperatures (up to 450 °C) with heat-resistant substrates have been positively tested as well. The photocatalytic coatings had to be activated by irradiation with UV-light.

3. RESULTS AND DISCUSSIONS

For comparison two routes for the fabrication of the nano anatase were investigated, the refluxing method and the hydrothermal method. The reflux route also was used for doping. The scheme of the preparation paths is shown in figures 1a and 1b.
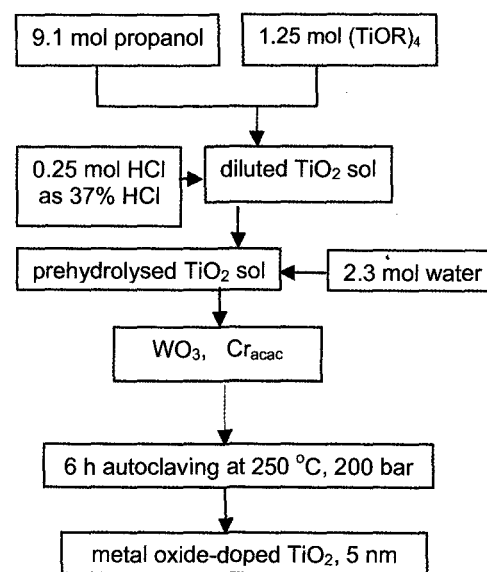

Fig. 1a: Hydrothermal synthesis of doped nano titania; acac: acetyl acetone

Pure redispersable nano titania was obtained if no dopants were used.
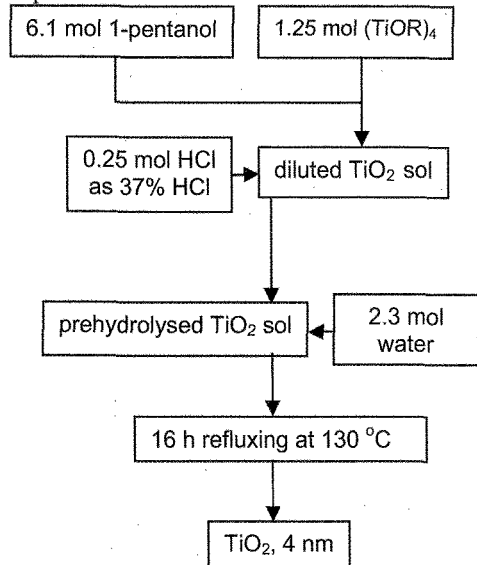
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┌─────────────────────┐  ┌──────────────────────┐
│  6.1 mol 1-pentanol │  │  1.25 mol (TiOR)₄    │
└─────────────────────┘  └──────────────────────┘
           │                        │
           └────────────┬───────────┘
                        ▼
┌──────────────┐  ┌────────────────────┐
│ 0.25 mol HCl │─▶│  diluted TiO₂ sol   │
│ as 37% HCl   │  └────────────────────┘
└──────────────┘            │
                            ▼
┌──────────────────────────┐  ┌──────────┐
│  prehydrolysed TiO₂ sol   │◀─│ 2.3 mol  │
└──────────────────────────┘  │  water   │
                │             └──────────┘
                ▼
┌──────────────────────────┐
│  16 h refluxing at 130 °C │
└──────────────────────────┘
                │
                ▼
        ┌───────────────┐
        │  TiO₂, 4 nm   │
        └───────────────┘
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Fig. 1b: Synthesis of TiO₂ nanoparticles by refluxing

In figure 2 the HRTEM micrograph of the nano-TiO₂ is shown.
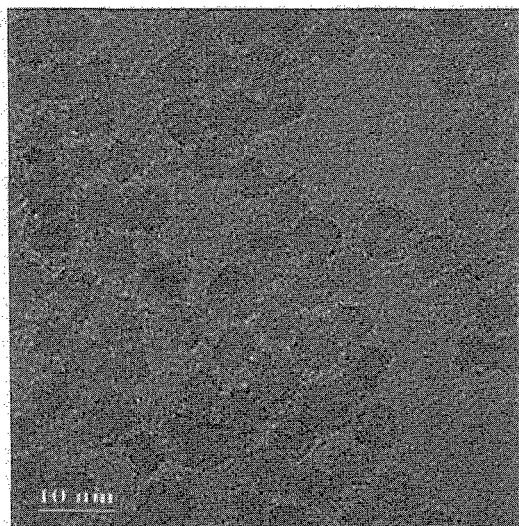
Fig. 2: HRTEM micrograph of hydrothermally synthesized TiO₂

One advantage of the described routes is that the TiO₂ is still covered by an alkoxy grouping containingcoating which makes it redispersable in organic solvents without any further treatment. The dried powder can be redispersed in pentane or alcohols. It also can be redispersed in water as it is shown in figure 3.
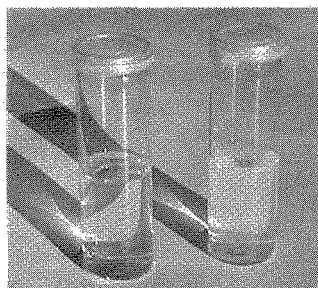
Fig. 3: Dispersions of unmodified ana-tase particles in wa-ter (right) and modi-fied (left) anatase particles in hydro-carbon solvent.

These sols were mixed with a so-called NANOMER® coating solution as described in figure 4.

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┌──────────────────────┐
│  TEOS, Si(ORₙ)X₍₄₋ₙ₎  │
└──────────────────────┘
           │◀────┌───────┐
           │     │  HCl  │
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│ NANOMER® Coating System   │
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           │     │ stable sol of │
           │     │ nano titania  │
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    │  coating sol   │
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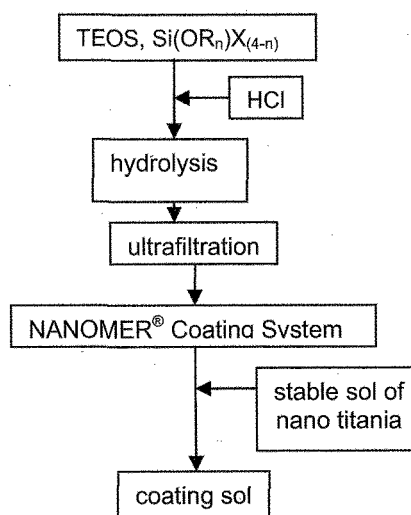
Fig. 4: Synthesis of the matrix material

The NANOMER® coating system was described elsewhere. It has been used for many applications so far outside of photocatalysis [11]. These matrix systems consist of nanoparticulate silica and hydrolysed silanes, forming an inorganic-organic hybrid network. The systems are cured at temperatures from 80 – 450 °C. Depending on the curing temperatures flexible systems for the application on sensitive substrates like plastics as well as glasslike systems on glass, metal or ceramics with a high abrasion resistance and anti-corrosion properties have been obtained. Other nanoparticulate materials were added to taylor material properties, e. g. TiO₂ to obtain photocatalytic properties. The advantage of this coating system is the relatively high content of inorganics, especially SiO₂ nanoparticles, which make the system rather stable against photocatalytic degradation. These systems have successfully been used for coatings on steel, for example, outside of the field of photocatalysis. For the investigations, the coating sol according to figure 1, in order to develop gradient coatings with photocatalytic activities only to be present on top of the system, the nanoparticles have to be surface modified with fluorosilane according to figure 5.
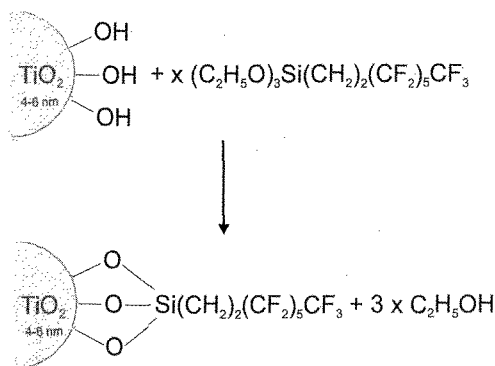
Fig. 5: Scheme of the surface modification of TiO_2 nanoparticles, surface modifier: FTS

For a good distribution of the surface modified nanoparticles in the organic liquid coating system the surface coverage with fluorosilane (FTS, tridecafluorooctyl-triethoxysilane) must not be higher than 40%. Above this limit, problems with miscibility take place, the critical micelle concentration (CMC) will be exceeded. Quantitative chemical analysis (vario EL III, elementar Analysensysteme GmbH) of the carbon content from remaining alkoxy groups of the synthesized nano anatase (under the assumption of spherical nanoparticles and a surface area of $1.8 \cdot 10^{-19}$ m² for hydroxyl or alkoxy groups) allows the calculation of the surface coverage of the anatase particles after the replacement of the alkoxy groups by FTS. For nanoparticles of a size from 4 to 6 nm a surface coverage of 15 to 24 wt.-% was calculated as an optimum, based on experimental results with different amounts of FTS. The idea for using the described gradient coatings was that due to the evaporation of the solvent, a decompatibilization of the particles and the system takes place and by thermodynamic drive they diffuse to the top of the system. This is indicated in the next figure. The results of a SIMS analysis of this process are shown in the figure 6. Here, we clearly can see that the concentration of the TiO_2 decreases significantly and is less than 1% at 0.6 mm. This is confirmed by the X-ray analysis as shown in fig. 7. Despite the low resolution of the X-Ray beam, the TiO_2 concentration of the is reduced by more than 50 % by switching from the lancing angle to the bulk. After coating, the surface is hydrophobic. In fig. 8, the effect of irradiation of the hydrophobic surface is shown: the contact angle to water decreases from 108° to < 10°. This can be interpreted by the oxidation of the C-C bonds of the fluorocarbon chains, as shown in fig. 9a and b.
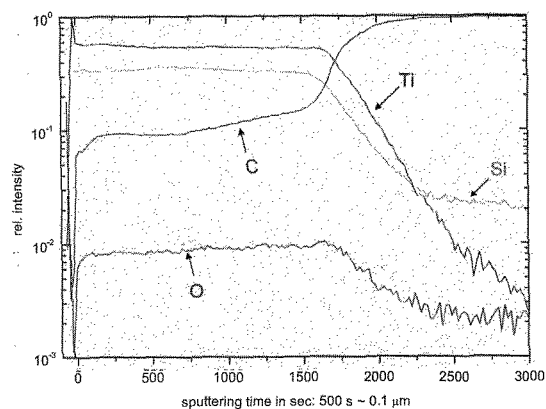

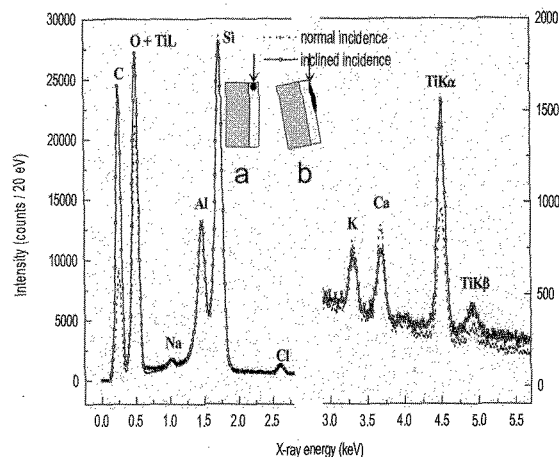Fig. 6: Gradient coating: SIMS analysis before photoactivation by UV-light

Fig. 7: Scheme of EDX analytical procedure:
a: normal incidence at layer cross section; b: inclined incidence (5°) at layer surface; material: TiO_2 + FTS; 15 keV [after Th. Krajewski]
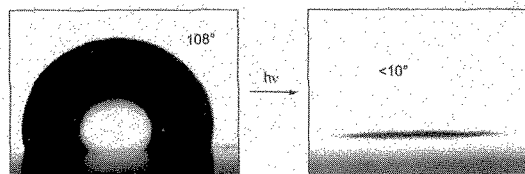

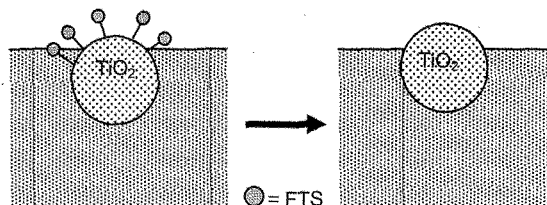Fig. 8: Contact angle before and after irradiation

Fig. 9a: Scheme: Degradation of FTS groups at the surface of the anatase nanoparticles
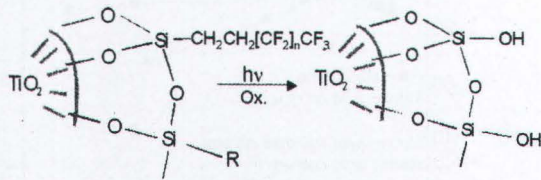

Fig.9b: Proposed mechanism: Photodecomposition of the modifying fluorosilanes during the first photoactivation

Due to the presence of SiO_2 nanoparticles, the silanes and the TEOS of the MTKS binder system, after the oxidative removal of the organics close to the TiO_2 nanoparticles, an inorganic barrier layer is supposed to be formed. During the observation period of several months of outdoor exposure, no decay of the layer system could be observed. This means, that a multiple gradient system is formed from a primarily homogeneous coating, as schematically shown in fig.10.
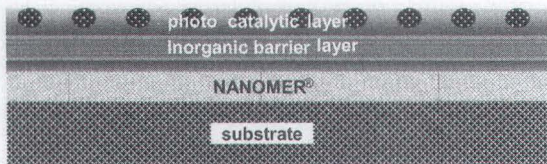
Fig. 10: Multiple layer formation

As it could be clearly seen from figures 6 and 7, the gradient formation with the TiO_2 on top of the layer has been formed rather well. This is attributed to the increasing decompatibilisation of the partially fluorine coated nanoparticle, since due to the loss of alcohols as solvent which act by polar molecules, the interfacial free energy between the hydrophobic TiO_2 nanoparticles and the OH-group containing sol-gel matrix is increased. Due to the small size of the TiO_2 nanoparticles, they are able to diffuse and once reaching the surface, they get upconcentrated and trapped there. The effect of a PC plate partially coated is shown in figure 11. The PC plate was dipped in a suspension of carbon black and removed from the liquid. After drying, the glass plate has been rinsed with water and as one can see, the right side gets completely clear without any traces of the carbon black whereas on the left side, the carbon black remains almost completely on the surface. Due to the hydrophilic surface on the right side of the plate, the soot could be rinsed off without any problems.
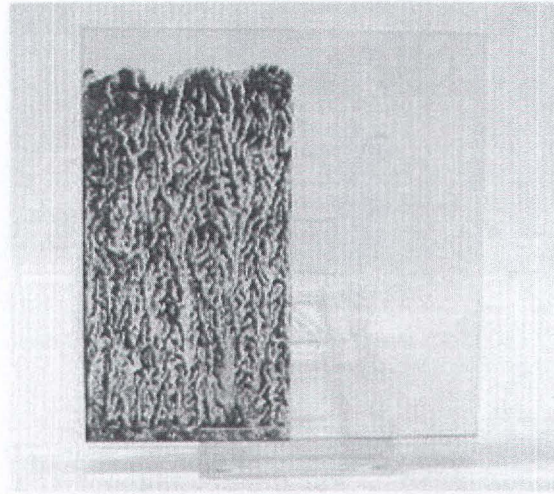

Fig. 11: After drying and washing with water – removal of carbon black applied by dipping a half-coated PC substrate into a suspension of carbon black in water

In figure 12, the first activation of coated PC plates is shown and the contact angle to water was determined. After preactivation with the beltron UV-radiator the contact angle decreases to a level below 10° (smaller angles could not be measured). Without preactivation, it takes four days in a HEREAUS suntester to reach a contact angle below 10° and in sunlight after eight days, the complete hydrophilicity is established.
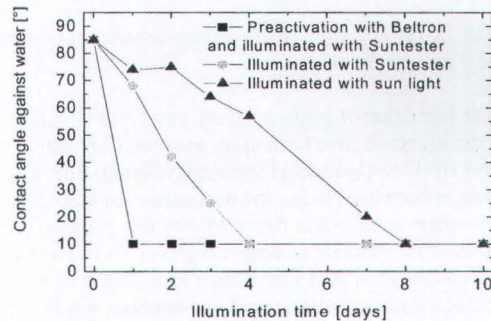

Fig. 12: Single layer photocatalytic systems coated on PC: activation by sun light and artificial light sources

In the following, two coating experiments have been carried out according to chapter 2.7. Chromium doped systems have been prepared by use of Cr(III) acetyl acetonate which was coprecipitated during the formation of TiO_2 nanoparticles using the reflux process. The effect of the chromium doping turns the nanoparticulate suspension into a yellowish colour as shown in figure 13.

Fig. 13: Undoped (left) and chromium(III) doped titania particles dispersed in toluene

X-ray investigations do not indicate any change between 1 and 5 % Cr(III) content and are almost identical to those of anatase, as shown in figure 14.
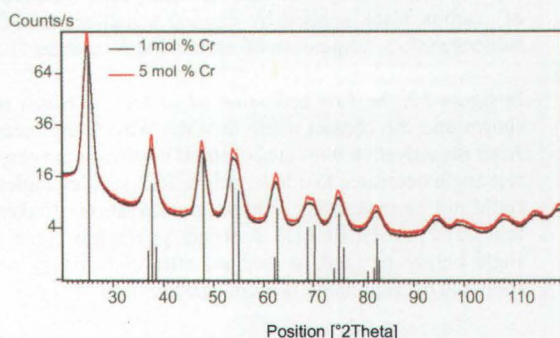

Fig. 14: X-ray spectrum of chromium doped titania with 1 and 5 mol-% of Cr(III)

For the formation of gradient layers, two types of surface modification have been used, once the FTS and second HDTMS (hexadecyl trimethoxysilane). Both systems have been used to test the degradation of stearic acid on glass as shown in figure 15. For this purpose samples of the gradient coatings on glass (10x10 cm²) and uncoated glass plates have been spin-coated with a saturated solution of stearic acid in n-heptane, it was found that nearly equal amounts of stearic acid were deposited on both surfaces (around 19 µg ± 15% stearic acid per cm² at a single coating step).
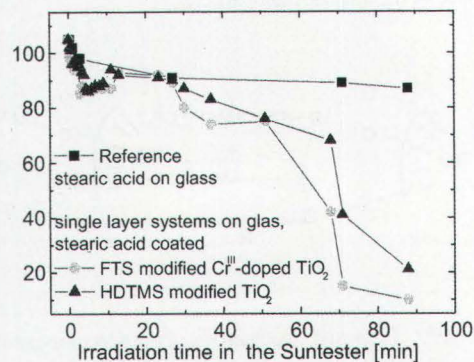
Contact angle against water [°]

Fig. 15: Photocatalytic degradation of stearic acid observed by the change in the contact angle against water

As one can see, the FTS coating of the chromium containing TiO₂ coating shows a higher decomposition rate which is attributed due to the better phase separation and an increased TiO₂ concentration on the surface. In figure 16, decomposition of methyl violet in water was tested. UV-irradiation was carried out through a filter with a sharp edge at 400 nm, that means only visible light was used. On the left side of figure 16, unmodified TiO₂ was used and no change in colour can be observed. On the right side, the chromium doped system was used which clearly shows a degradation of the dye with visible light. This shows that the doping with chromia leads to a visible with catalytic activity.
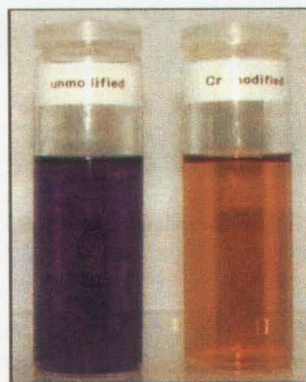

Fig. 16: Undoped and chromium doped titania sols in water, after addition of methyl violet and irradiation with visible light ($\lambda > 400$ nm)

However, it's not quite clear how the chromium is incorporated in the TiO₂ so far. This will be closely investigated in future. These experiments show at first, that the doping of the chromium leads to a visible light effect and second, the coating of the chromium doped TiO₂ nanoparticles leads to the gradient formation in a similar way as it has been demonstrated with undoped systems. Another type of "doping" was used by the introduction of WO₃ particles into the TiO₂ containing suspension. In this case, however, in opposition to the chromium not molecular, but particulate systems have been used and the tungsten(VI) oxide particles in the sub-µm size, that means between 2 and 300 nm in diameter. In figure 17a

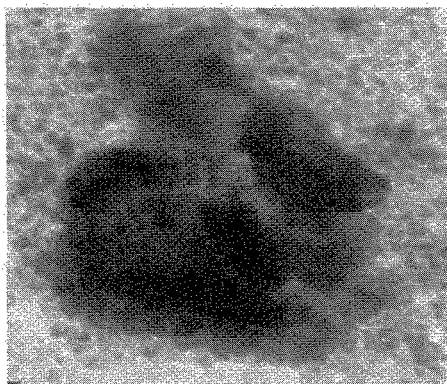to 17c, the reaction of WO_3 in various concentrations of TiO_2 was shown.
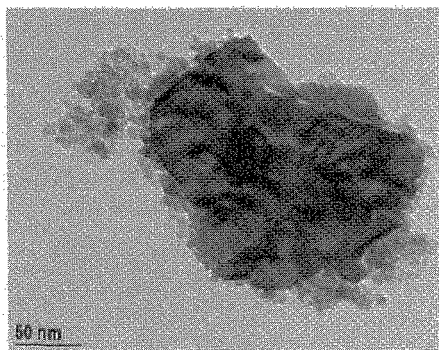

Fig. 17a: nano anatase on WO_3 1 mole-% WO_3
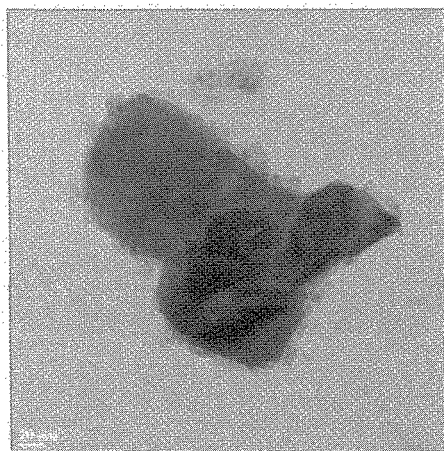

Fig. 17b: nano anatase on WO_3 5 mole-% WO_3

Fig. 17c: nano anatase on WO_3 10 mole-% WO_3

In 17 a the lowest and in 17c the highest concentration of WO_3 is shown. As one clearly can see is that the TiO_2 is deposited around the WO_3 sub-µm particles. Especially at the high concentrations, the WO_3 particles are nicely coated by the TiO_2. In figure 18, the X-ray defrac-

tion patterns are shown indicating crystalline WO_3 at a very low concentration.
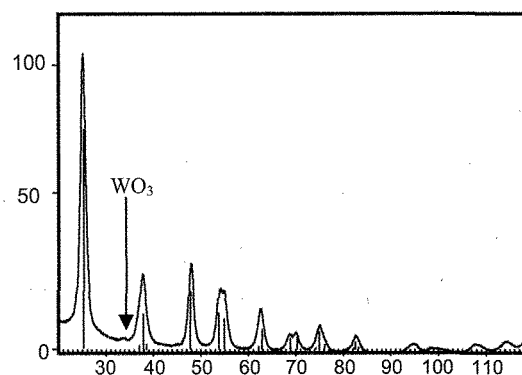

Fig. 18: XRD-reflex of WO_3 in a tungsten doped nano anatase (5 mol-% WO_3 added)

Screening tests in suspensions have been carried out by the decomposition of rhodamine B. The results are shown in figure 19.
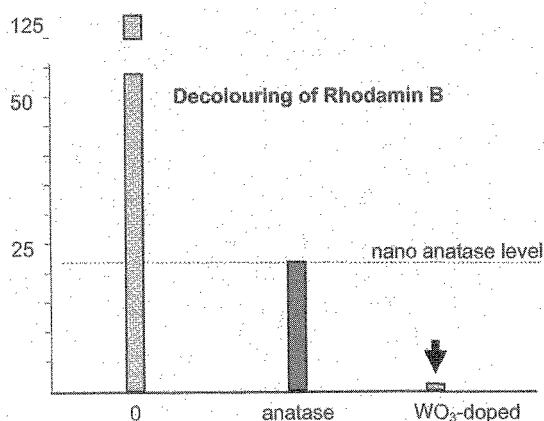

Fig. 19: Photocatalytic degradation of rhodamine B using undoped anatase and anatase deposited on WO_3.

As one clearly can see is the TiO_2 deposited on the tungsten oxide shows the significantly higher decomposition activity compared to pure anatase. This can be attributed to the electronic effect of tungsten oxide as a semiconductor which is also able to trap electrons and increasing the recombination time of the electron-hole pair formation. This will be more investigated in more details in the future, too.

3. CONCLUSION

As a conclusion, the following can be stated: The doping and the interaction of particulate components, such as tungsten oxide with nanoanatase, leads to additional activity effects and has to be investigated in details. The molecular type of doping with chromia not necessarily leads to the reduction of the activity as indicated by Hermann [12], but also leads to a visible light effect. By

coating of the nanoparticulate systems with hydrophobic or oleophobic components, the gradient formation can be obtained and especially if highly inorganic NANOMERS® are used, very stable systems can be obtained in a single-step coating technology.

ACKNOWLEDGEMENT

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