HYGIENIC COATINGS

TiO_2 Nanoparticle Coatings for Self-Cleaning and Antimicrobial Application

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Paper 20

TiO_2 NANOPARTICLE COATINGS FOR SELFCLEANING AND ANTIMICROBIAL APPLICATION

Abstract

The photocatalytic effect of TiO_2 (especially anatase) is very well known. For the utilization of this effect for hygienic surfaces, especially on plastic surfaces, a wet coating technology has been developed. To enhance the photocatalytic effect of TiO_2, anatase nanoparticles with a narrow volume particle size distribution (d_{10} = 7 nm, d_{50} = 9 nm, d_{90} = 11 nm) have been synthesized and surface modified by hydrophobic components in order to disperse them in organic solvents. Since the photocatalytic effect is a non-specific one, and all organic materials are oxidized, a buffer layer stable against oxidation has been used between plastic substrates and TiO_2 top layer. The selfcleaning behaviour was determined by the degradation of bovine serum albumin. After 8 h under irradiation (1200 W/m^2) in a sun tester the concentration was decreased from 0.3 mg/cm^2 under the limit of detection. To show the antimicrobial effect colony forming bacteria (E. coli) were determined after 10 min irradiation (1200 W/m^2) leading to an inactivation of about 50 % of 1000 CFU/cm^2. Additionally the coated plastic surface shows an antifogging behaviour.

Introduction

The disinfection of contaminated surfaces and the degradation of toxic or environmentally problematic organic materials are problems of great importance in hospitals. Photocatalytic coatings based on TiO_2 are able to oxidize unspecifically every organic material [1]. The mechanism of photocatalysis in presence of TiO_2 occur by absorbing UV-sunlight indicating electron transfer reactions and hydroxyl radical generation at the TiO_2 surface [1, 2]. These radicals are responsible for micro-organism inactivation by induced surface oxidation of the cell wall and the degradation of all organic materials on the activated surface.

For this reason photocatalysis [1, 2] is shifted worldwide in the centre of interest of industrial as well as institutional researchers. The growing interest in photocatalytic applications with TiO_2 is documented in the exponential growth of the world-wide patent applications over the last decade.

State-of-the-Art coatings are either not transparent, needs high temperature to form photocatalytic layers with sufficient activity or had other properties limiting possible applications especially on transparent polymer substrates [3 - 6]. For being mostly flexible in coating surfaces of different materials, a complete system comprising of a carrier layer with several functions and an active TiO_2 layer (anatase phase) has to be developed [7 - 9]. One focus of worldwide interest is laid on a possibility to use thermal sensitive substrates like plastics, textiles, etc. If the active phase is not allowed to be thermally treated on the substrate, the well-crystallized anatase phase has to be synthesized before carrying out the coating process.

The objective of the present work was to develop a transparent two-layer system, which covers a wide range of substrates, especially on plastic surfaces. The system shall be based on a carrier layer [10 - 13], which functions as adhesion promotor, as diffusion barrier for metal ions disturbing the photocatalytic process and as protection of substrates made of organic materials that should not be degraded by photocatalysis. The active top layer has to be made of crystalline TiO_2 (anatase phase) without exposing the substrate high temperatures and with high photocatalytic activity needed for the self-cleaning and disinfection process.

Experimental

Commercially available (Goodfellow) DIN A4 size Polyethylenterephthalat (PET) and Polycarbonate (PC) foils with thicknesses of 100...200 µm were used as substrates. The carrier layer is synthesized of alkyl alcoxy silanes, Tetraethylorthosilicate and surface modified SiO_2 (> 25 wt. %) [10]. The resulted sol was applied by dip-coating on the plastic substrates and heated for 1 h at 80 °C.

To form the photocatalytic top layer Anatase nanoparticles were synthesized in a first step. Titania alkoxide was hydrolysed in alcoholic solution. After 2 h stirring at room temperature the solvent and by-products were distilled under reduced pressure. The resulted resinous substance was dispersed in absolute 1-propanole an was heated in a lyothermal treatment at 250 °C under 200 hPa for 6 h. After centrifuging and distillation under reduced pressure crystalline nanoparticlulate anatase was obtained.

Afterwards the nanoparticles were surface modified with organically modified alkoxysilanes to obtain a good re-dispersibility in different solvents and to act as a

flexible matrix on the substrate. This sol was applied on the plastic substrates by dip-coating and heated for 1 h at 100 °C. The coating was activated by irradiation with UV light (max. at 200 nm) for 5...10 min.

The crystallisation of the TiO_2 nanoparticles was investigated by High Resolution Tunnel Electron Microscope (HR-TEM) including Selected Area Electron Diffraction (SAED) with a CM 200 FEG from Philips and the particle size distribution by Photon Correlation Spectroscopy (PCS) with an ALV 5000 MTDC from ALV GmbH. The particle distribution in the photocatalytic layer was characterised by HR-TEM and the reaction mechanism during activation by IR-Spectroscopy with an IFS 25 from Bruker.

To determine the protein degradation 10 ml of defined protein solutions (0.75 mg/ml bovine serum albumin, Sigma) were given into a petri dish containing a coated sample or uncoated reference of 5 x 5 cm^2, respectively. The samples were illuminated with a suntester SUNTEST CPS (Heraeus) for 2...8 h at maximal light intensity (1200 W/m^2). Protein concentration was determined after reaction with Bradford reagent (Sigma) at a wavelength of 600 nm (Biophotometer, Eppendorf). The remaining volume after illumination was determined and the protein concentration was referred to the original volume.

For the determination of the microbial effect of functionalised and not functionalised surfaces, the Gram negative bacterium *Escherichia coli* 498 was obtained from the German Collection of Micro Organisms and Cell Cultures (DSMZ) and cultivated in M1 medium (5 g/l peptone, 3 g/l meat extract, 15 g/l agar if necessary, pH = 7).

Two different preparation methods for the bacteria were used

1. Liquid suspensions with *E. coli* were diluted to give about 10.000 colony forming units / ml. 100 µl of this inoculum was distributed equally over the agar surface. The samples were placed on the inoculated surface and illuminated in the suntester SUNTEST CPS (Heraeus) at maximal light intensity (1200 W/m^2) with a xenon lamp for 10 minutes. The samples were removed from the agar surface and the number of colony forming units (CFU) was determined after incubation at 30 °C.
2. Liquid suspensions with *E. coli* were diluted to give about 10.000 colony forming units / ml. 15 ml of this solution was added to coated and uncoated samples of 5 x 5 cm^2 in petri dishes. The samples were illuminated for 10 minutes,

respectively. 100 µl of the liquid was distributed on agar plates and the number of the colony forming units (CFU) was determined after incubation at 30 °C. Mean values of three CFU determinations are given.

Results and Discussion

Investigating the particles after the lyothermal treatment by TEM show their crystallinity and the size of about 10 nm. SAED measurements show the anatase phase and PCS the narrow volume particle size distribution (d_{10} = 7 nm, d_{50} = 9 nm, d_{90} = 11 nm). This characterisation is described elsewhere in more details [14].
In the suntester, the samples are subjected to radiation, which can generate radicals in the case of TiO_2-coated samples to initiate protein degradation or inactivation of micro organisms. The effect of coated and uncoated samples (illuminated reference) was examined in a suntester at about 1200 W/m². The protein concentration after different hours of illumination is shown in Fig. 1.

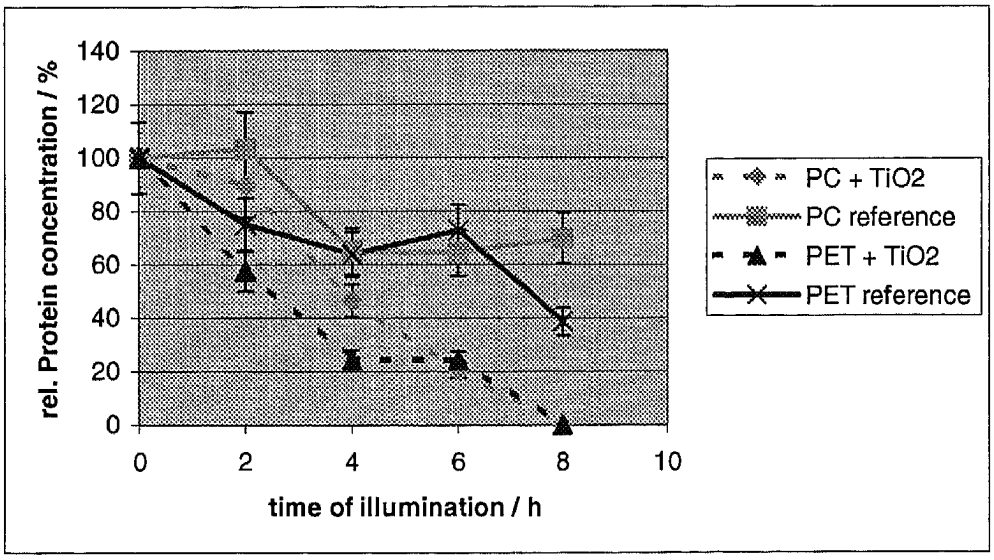

Figure 1: Protein concentration after incubation of liquid protein samples (0,75 mg/ml bovine serum albumin) in the suntester. 10 ml protein sample was illuminated with 5 x 5 cm² PC samples, reference: uncoated PC film.

In Fig. 1 the degradation of bovine serum albumin during incubation in a sun tester was shown. After 8 h around the half of the proteins were degraded on the uncoated reference substrate, while on coated PC and PET substrates no proteins could be detected after that time. It is assumed that the degradation on uncoated polymer foils is caused by the irradiation in the sun tester.

The number of colony forming units (CFU) decreased after an irradiation time of 10 minutes as shown in Figure 2 (method 1) and Table 1 (method 2).

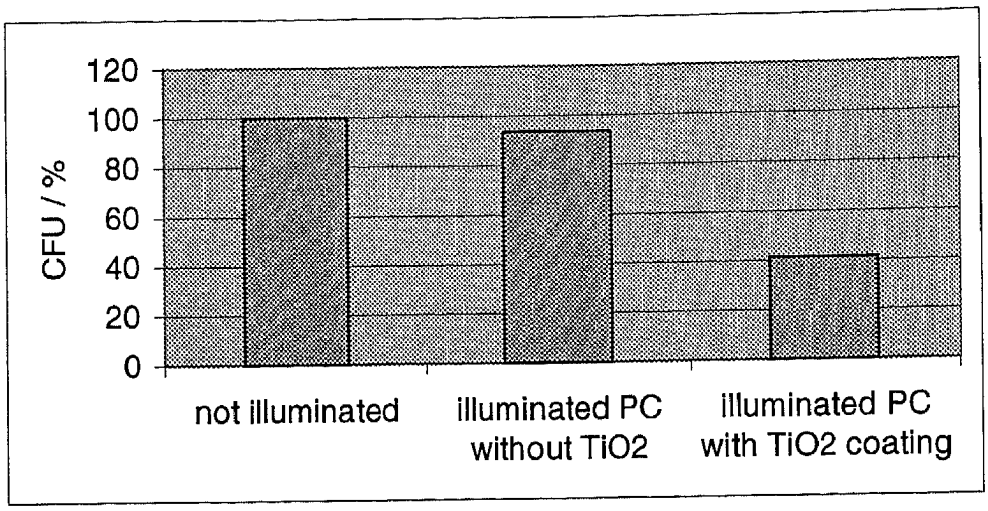

Figure 2: Colony forming units (CFU) of *E. coli* on agar plates (method 1) covered with sample films; coated and uncoated PC films were placed on the incubated agar plates and illuminated for 10 min.

Table 1: Colony forming units (CFU) of *E. coli* (method 2) after illumination of 15 ml of diluted liquid medium with 5 x 5 cm^2 PC film with and without TiO_2 coating.

Substrates	CFU after 10 min
Reference (not illuminated)	100,0 %
PC reference	70,1 %
PC + TiO_2	40,7 %
PET reference	51,4 %
PET + TiO_2	44,6 %

As shown in Fig. 2 and Table 1 the number of colony forming bacteria could be significantly reduced during the incubation time. The high reduction on uncoated PET substrates could be explained by the assumption that the PET surface was changed during irradiation reducing the adhesion of the bacteria.

A high activity of protein degradation and inactivation of the bacterium *E. coli* was achieved after short times of irradiation. As the number of CFU on the not covered area of the agar plates is comparable, the inactivation is not due to different illumination intensities but is an effect of the TiO_2 coating.

Additionally the photocatalytically coated polymer foils exhibit anti-fogging properties as shown in Fig. 3

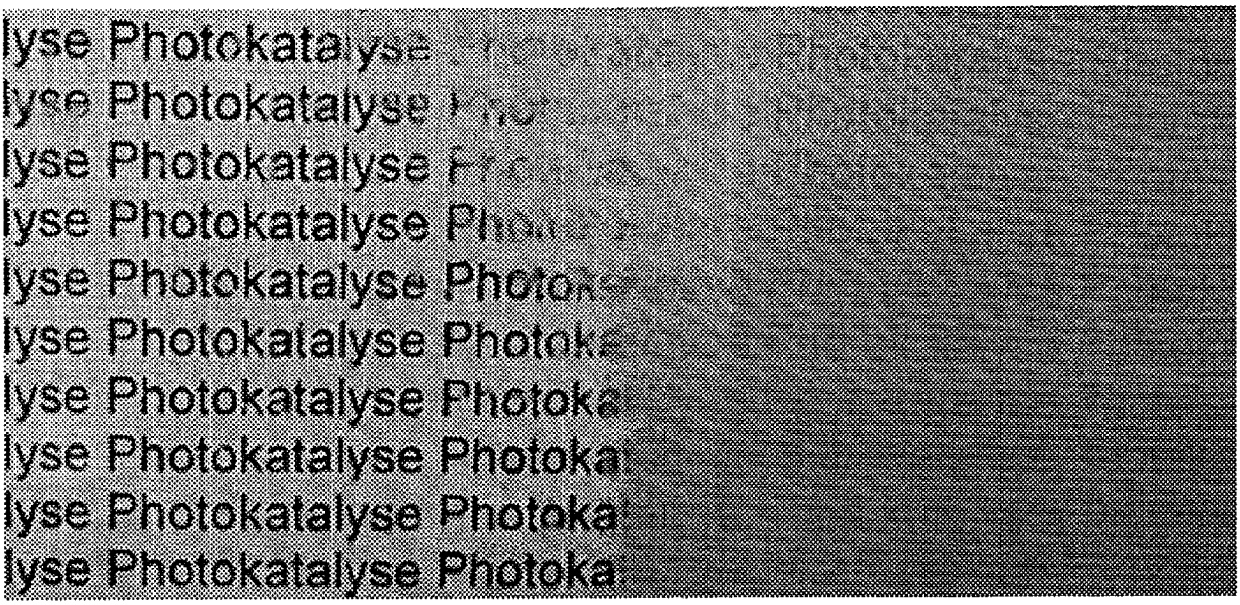

Figure 3: Anti-Fogging behaviour of a photocatalytic coating on a polymer foil. Water spreads on the irradiated side (left) in a water steam.

In Figure 3 the anti-fogging behaviour of a photocatalytic coating on polycarbonate is illustrated. After the coating and curing step only the left side was activated by irradiation with UV-light. The surface is getting hydrophilic (contact angle against water < 5 °) and light passes unhindered through this part when the sample was held in water steam.

Conclusion

Nanocrystalline anatase particles with high photocatalytic activity could be synthesised. A two-layer concept was realized to coat different substrates especially thermal sensitive polymer foils. A high activity of protein degradation and inactivation of the bacterium *E. coli* was achieved after short times of irradiation. Additionally the photocatalytically coated polymer foils exhibit anti-fogging properties Current research focuses on the improvement of the mechanical performance of titania-coatings with preservation of the high photo-activity via fixation of the particles in an adapted inorganic matrix.

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