PLASMA CURING OF WET CHEMICAL DEPOSITED LAYERS FOR ANTIBACTERIAL AND PHOTOCATALYTIC SURFACES

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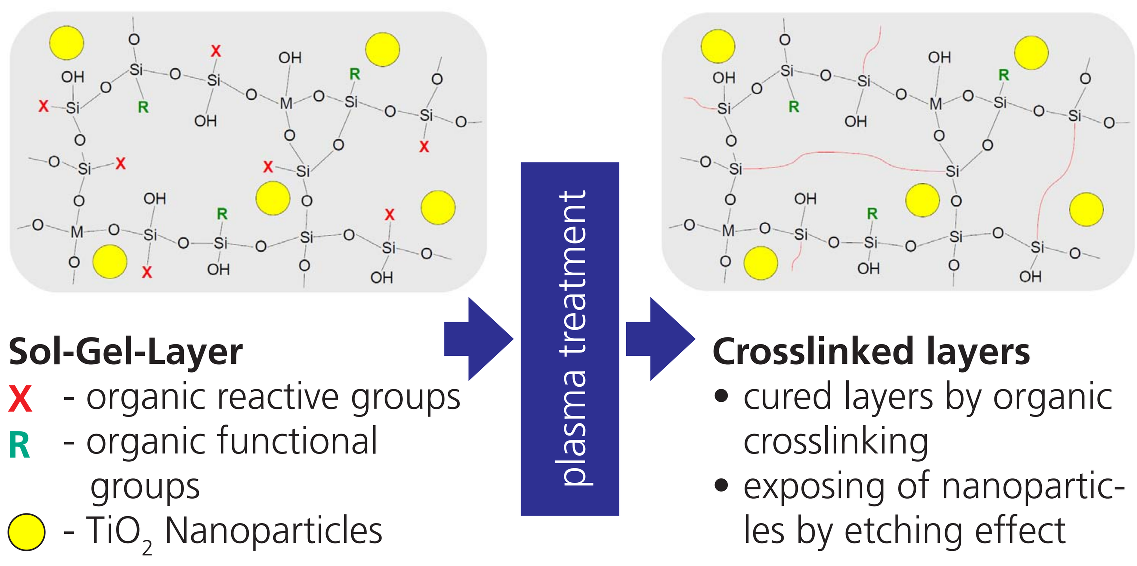
ABSTRACT

TiO_2 in the anatase modification is a well-known photocatalytic material, that shows photoinduced hydrophilicity and photocatalytic induced oxidation and reduction reactions during UV-A irradiation. One possibility for the fabrication of photocatalytic coatings is the use of nanoscale TiO_2 particles. A combined wet-chemical and plasma based coating method was developed, that applies hybrid polymer precursors with immersed TiO_2 nanoparticles on atmosphere and uses a low pressure plasma for curing of the layers. During the plasma treatment, curing is achieved simultaneously with the crosslinking of the layer. Additionally, the plasma etching effect partially exposes buried TiO_2 nanoparticles to the surface.

In this paper, the plasma curing process and corresponding investigations regarding different hybrid polymer precursors, plasma parameters and layer properties will be presented. Investigations regarding photocatalytic properties include decomposition of methylene blue and of pharmacological substances as well as reduction of microbial colonization.

EXPERIMENTAL

PLASMA CURING OF HYBRID MATERIALS

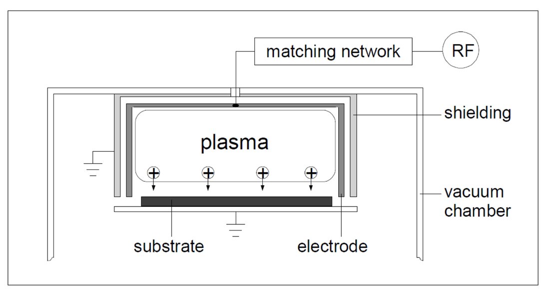


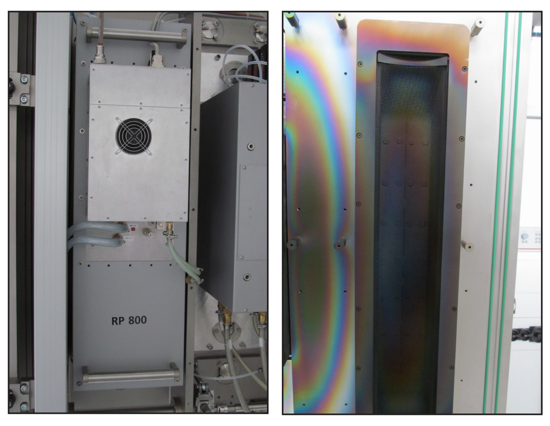
Sol-Gel-Layer
X - organic reactive groups
R - organic functional groups
- TiO_2 Nanoparticles

Crosslinked layers
- cured layers by organic crosslinking
- exposing of nanoparticles by etching effect

- inorganic-organic hybrid materials: ORMOCER®
- plasma curing of hybrid layers possible for coating systems for glass, stainless steel and plastic substrates

PLASMATREATER TECHNOLOGY FOR CURING OF HYBID LAYERS



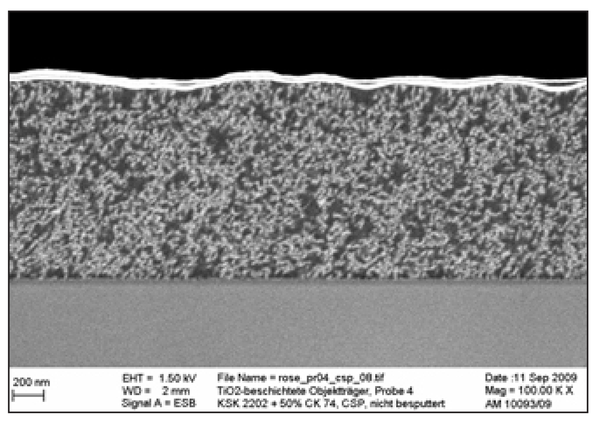


The plasmatreater works with:

excitation:	RF; Frequency 13.57 MHz
process pressure:	5×10^{-4} to 5×10^{-3} mbar
substrate dimension:	up to 700 mm width
power source:	up to 5 kW

INCORPORATION OF PHOTOCATALYTIC ACTIVE TiO_2 NANO PARTICLES

- synthesis of TiO_2 nanoparticles by Fraunhofer ISC (size: 30 nm, homogen dispersible in hybrid matrix material, colorless, highly photocatalytic active
- plasma curing of hybrid matrix with dispersed nanoparticles proven (mass ratio: up to 50% without degradation of layer hardness by particles)
- no release of nanoparticles of the cured layers (proven by particle analysis)

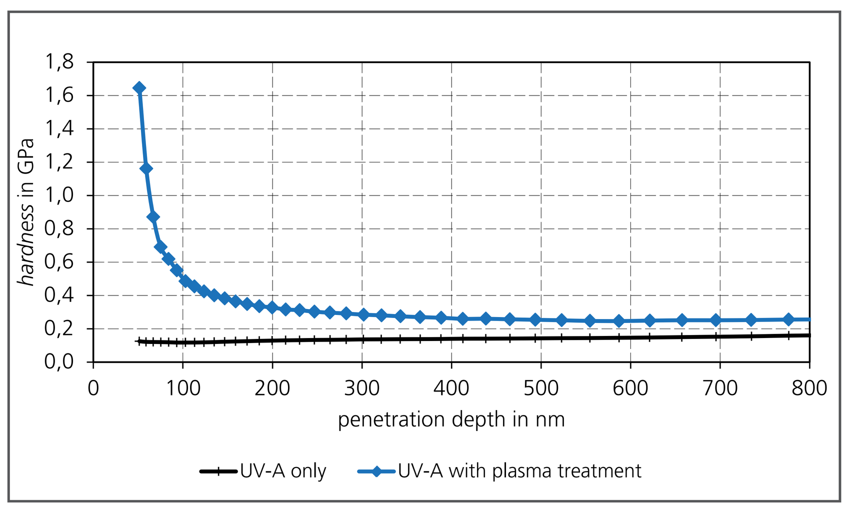


SEM analysis of TiO2 nanoparticles in hybrid matrix

RESULTS

PLASMA BASED CURING OF THE LAYERS

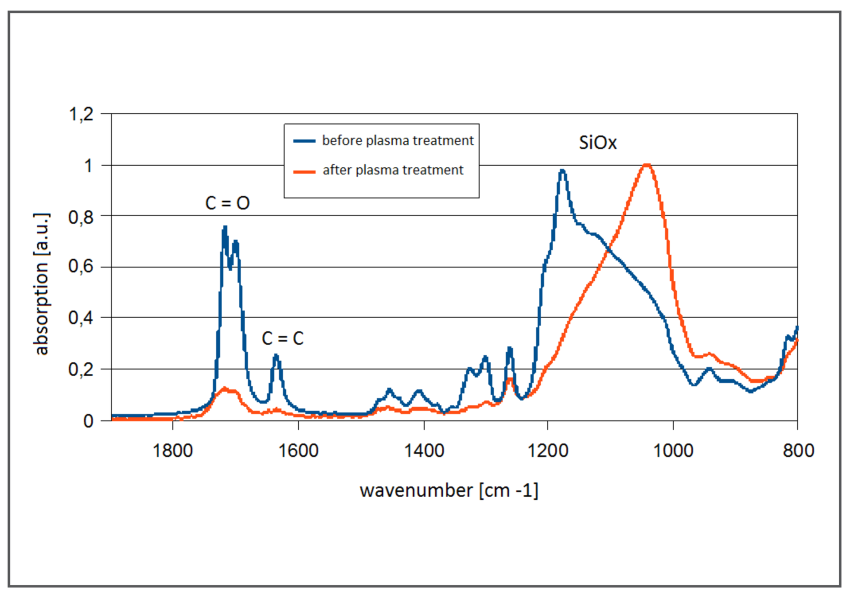
Curing of hybrid polymer layers by means of plasma treatment
(standard methode of curing: treatment of samples by UV irradiation)
- strong increase in the hardness on surface by plasma treatment
- increase in hardness also in the bulk:
  - start of the polymerisation on the surface by direct plasma exposure; formation of radicals
  - crosslinking by following polymere chain reaction



Nanoindentation of a plasma cured layer

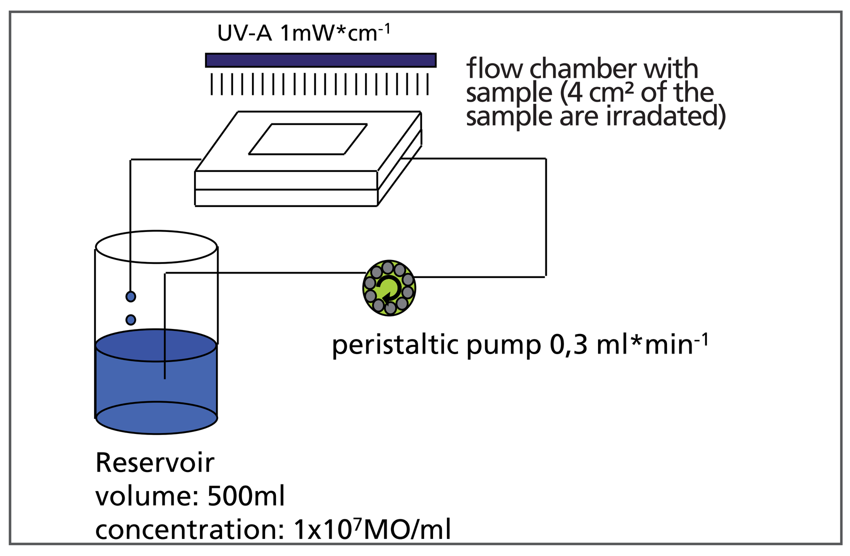
Proof of curing by fourier transform infrared spectroscopy (FTIR) (measured in reflection):
- reduction of the organic double bond (C=O; C=C)
- creation of SiO_x bonds

wavenumber [cm-1]	chemical bond
1720 / 1700	C = O
1640	C = C
1120 - 1020	Si - O -Si
1270 - 1260	Si - CH_3

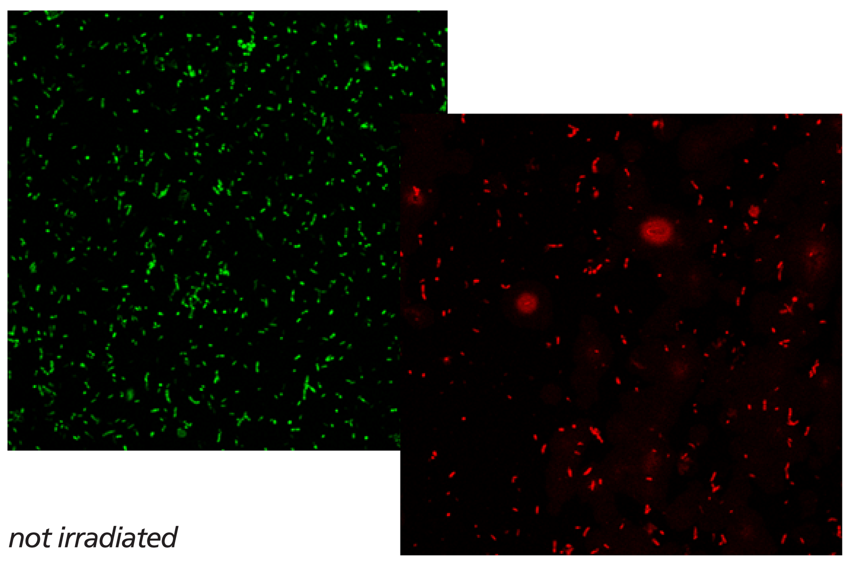


BIOFILM FORMATION

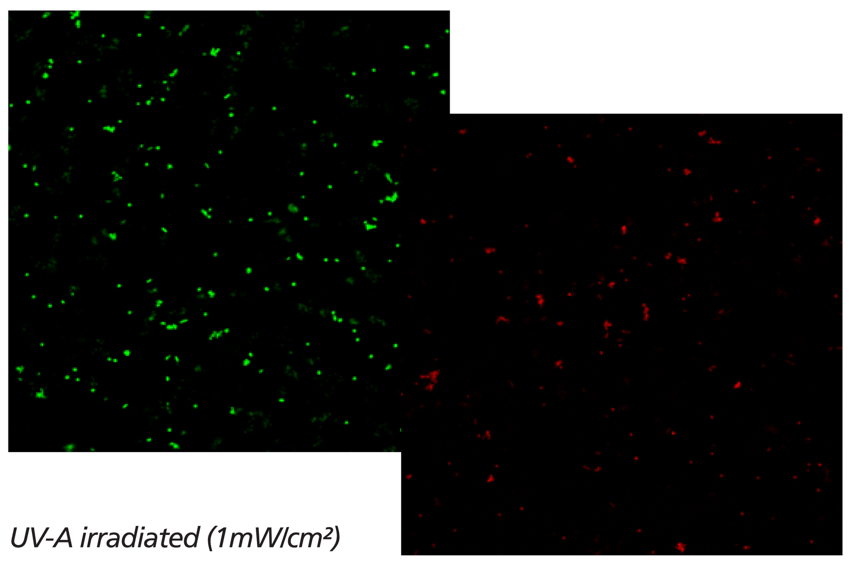
- models for micro-organisms: river water, drinking water and infection
- exposition of nanoparticles on the substrate surface by preconditioning of the layers with UV-B radiation (proof by contact angle measurement as well as AFM analysis)
- the bio-adhesion testing demonstrated a reduction of adhesive microorganisms on irradiated samples
- the coated layers are photocatalytical active and lead to a reduction of the bacterial adhesion and bio film formation



Schematic flow chamber of iba Heiligenstadt e. V.



not irradiated



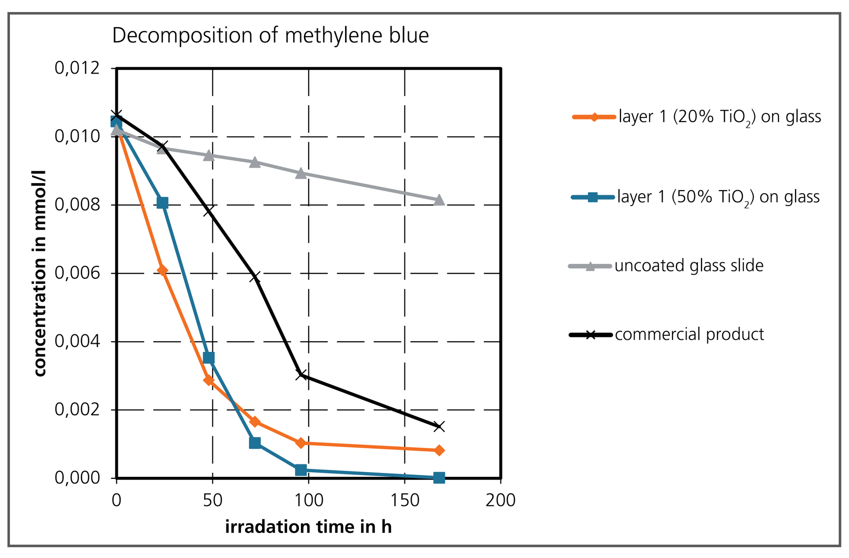
UV-A irradiated (1mW/cm²)

Bacteria have been inked to make visible (green): living cells (red): dead skin cells

PHOTOCATALYTIC ACTIVITY

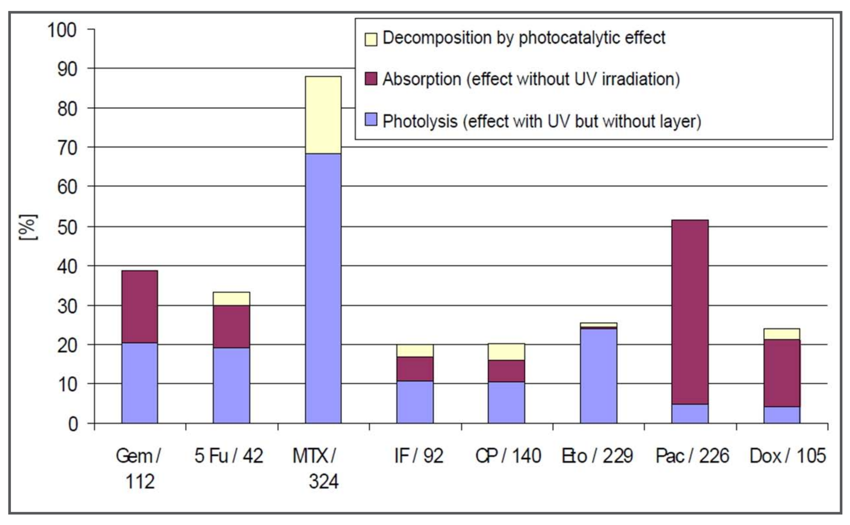
Decomposition of methylene blue
(UV-A irradiation: 1 mW/cm²)
- high photocatalytic activity of layers with TiO_2 particles
- better results as a commercial product (photocatalytic coated glass)

- water contact angle measurement show a hydrophilization of coatings by UV-B irradiation



DECOMPOSITION OF CYTOTOXIC AGENTS

- cytotoxic agents are toxic, mutagenic, carcinogenic, toxic for reproduction
- investigation of decomposition by chromatography
- decomposition was proven, under consideration of absorption (effect without UV irradiation) and photolysis (decomposition by UV irradiation, only)



CONCLUSIONS

A combined wet-chemical and plasma based coating method was developed, that applies hybrid polymer precursors with immersed TiO_2 nanoparticles on atmosphere and uses a low pressure plasma for curing of the layers.
- curing without the addition of UV initiators
- shorter process times and lower process temperature than necessary for thermal curing process
- curing is possible even on temperature sensitive substrates

Addition of TiO_2 nanoparticles was possible up to a mass ratio of 50%. These layers show high photocatalytic activity (decomposition of MB and of cytotoxic agents) and a significant decrease in bacterial adhesion and in the biofilm formation.

Possible applications include medical devices, environmental engineering and coating of surfaces for antibacterial activity or easy to clean applications.

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