PHOTOCATALYTIC ACTIVE COATINGS-ENVIRONMENTAL WAY TO IMPROVE QUALITY AND DURABILITY OF BUILDINGS

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Abstract

Transparent coatings of TiO_2-SiO_2 nanocomposite were developed to be applied on building facades in order to prevent growth of microorganisms and thus to improve urban building sustainability. Structure and texture characteristics of the prepared nanocomposites were determined by electron microscopy (SEM, TEM + EDS), their photocatalytic activity was quantified by testing self-cleaning ability and antimicrobial activity. The self-cleaning properties were evaluated according to the standard ISO method based on photocatalytic degradation of methylene blue. The TiO_2-SiO_2 nanocomposite coatings were applied on various types of substrates commonly used in building industry. The antimicrobial activity was mainly investigated for algae because these microorganisms are often responsible for facades ageing. According to the laboratory tests the prepared TiO_2-SiO_2 nanocomposites are highly efficient. This fact was already proved by first applications in real conditions. The transparent SiO_2-TiO_2 nanocomposites represent an ecological and noninvasive way how to keep nice appearance of buildings for a long time. It is due to their permanent photocatalytic activity causing self-cleaning and algicidal effects. Such coatings may significantly reduce ageing processes on facades of buildings that are caused by microbiological pollution and smog exhalations.

Keywords: SiO_2-TiO_2 nanocomposite, photocatalysis, photocatalytic paint, self-cleaning surfaces, photocatalytic algae degradation

1. INTRUDUCTION

The aging of buildings is a complex process caused by chemical, physical and biological factors. In addition to the impact of weather influence (sunshine, rain, wind, frost, temperature changes etc.) and air pollutants the formation of biofilms on the building surfaces is one of the main factors of building aesthetic changes and deterioration.

Microbiological organisms are known to produce acids which can react chemically with the building materials. Algae, moss and lichens form humus in which larger and more damaging plants can grow. It subsequently increases retention of moisture in the building material. Such deteriorating processes are accelerated even by atmospheric pollutants, which in combination with air moisture form a corrosive mixture [1]. The photocatalytic protective layer is able to prevent biofilms growth due to their permanent oxidative decomposition. The recent research of novel photocatalytic paints indicates that such applications represent a promising environmental way how to prolong the service life of buildings [2].

The photocatalytic properties of semiconductors are based on the photogeneration of separated charge carriers, positive holes (h^+) and electrons (e^-), which occurs upon the absorption of light corresponding to the band gap [3, 4]. The formed electron-holes pairs can subsequently either recombine or initiate redox reactions on the photocatalyst surface. The reductive and oxidative ability of the photogenerated electrons and positive holes, respectively, are determined by the potentials of corresponding conduction and valence band [5]. Processes occurring within the semiconductor particle upon irradiation are illustrated in **Figure 1** [6].

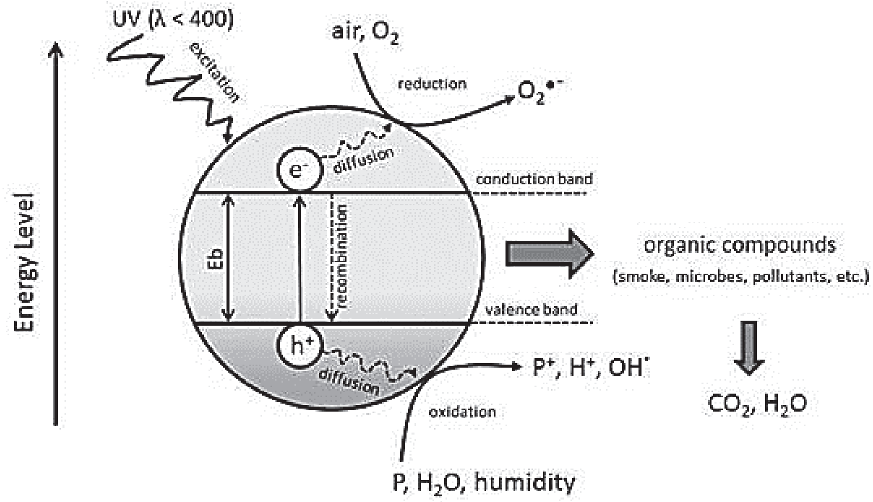

Figure 1 Illustration of photocatalytic processes occurring on semiconductor particle upon irradiation

Titanium dioxide (TiO_2) in anatase crystalic form is he most common photocatalyst. Its band gap energy is 3.2 eV. This material is inexpensive, non-toxic and chemically stable. The photogenerated positive hole shows a strong oxidizing ability. Therefore photocatalytic properties of anatase have been extensively investigated, especially its promising applications concerning degradation of environmental contaminants [7-9] or inactivation of biological pollutants [10-12].

2. EXPERIMENTAL

2.1. SiO_2-TiO_2 nanocomposite coating

The photocatalytic composite paint consists of a photocatalyst and a binder. The nanocomposite was prepared in form of aqueous dispersion containing 1 - 3% of dry matter formed by 40 wt.% of TiO_2 (with the size fraction of TiO_2 particles 5 - 100 nm) and 60 wt.% of SiO_2 (with the size fraction of SiO_2 particles 5 - 50 nm). For material characterization of the composite, samples prepared by spraying the aqueous dispersion in liquid nitrogen and immediate lyophilisation of the frozen droplets at temperature - 60 °C and pressure 1.3 kPa. The obtained dry composite was characterized by electron microscopy (SEM, TEM and EDS).

2.2. Photocatalytic activity determination

2.2.1. Self-cleaning properties

The photocatalytic self-cleaning properties of the prepared composite coatings were determined using an ISO 10678:2010 standard method based on photocatalytic degradation of methylene blue [13]. Aqueous solution of methylene blue (MB) is decoloured in contact with the photoactive surface under UV irradiation. The used intensity of UV-A radiation (BLB λ = 365nm) was 10 ± 0.5 W/m^2. The amount of MB dye remaining in the solution was determined by absorbance measurements at λ = 640 nm by UV/Vis absorption spectroscopy (Perkin-Elmer Lambda 35).

The composite coatings were applied on different types of supports: lime, silicone, acrylate and silicate plasters. The size of tested samples was 5 cm x 5 cm. Each sample was first preconditioned in more concentrated MB solution (c = 20 μmol/l) for 12 hours to avoid decrease of MB concentration due to adsorption during the testing. The conditioned samples were subsequently tested using less concentrated MB solution (c_0 = 10 μmol/l).

2.2.2. Antimicrobial properties - algae degradation

The antimicrobial activity of the prepared TiO_2-SiO_2 nanocomposite coatings was based on the photocatalytic degradation of *Chlorella vulgaris* (strain of H1955) algae. *Chlorella vulgaris* was cultivated on a BBM medium at room temperature.

The TiO_2-SiO_2 nanocomposite coatings on pieces of white marble and lime plaster were prepared by immersion of the sterilized pieces of these supports into nanocomposite suspension for 30 s. The dried substrates were put in Petri dishes with sterile agar layer on its bottom. Next 3 µl of Chlorella vulgaris suspension was pipetted on the prepared substrates. The Petri dishes with algae on substrates were finally sealed to prevent evaporation of the agar layer and put into a special photoreactor. To avoid any contamination of the samples, all these preparations were performed in sterile flow box. The plastic material of Petri dishes was transparent for visible light as well as UVA radiation. The spectral composition of light applied in the photoreactor was adjusted to simulate solar radiation with intensity of 1 mW/cm^2.

3. RESULTS AND DISCUSSION

3.1. SiO_2-TiO_2 nanocomposite coatings characterization

Coatings prepared from the TiO_2-SiO_2 nanocomposite colloidal suspension were transparent. The used suspension was stable. A potential sediment could be easily resuspended by short shaking.

The SEM and TEM micrographs of the TiO_2-SiO_2 nanocomposite are shown in **Figure 2**. Isolated islands of titanium dioxide photocatalyst (lighter objects on the left micrograph) placed in SiO_2 matrix (darker colour on the left micrograph) can be seen. The other TEM micrograph also confirms the formation of TiO_2 aggregates (darker objects on the right micrograph) surrounded by lighter SiO_2 matrix. It is evident from these micrographs that the SiO_2 nanoparticles form a matrix that separates agglomerated TiO_2 nanoparticles and thus prevents a direct contact of the TiO_2 photocatalyst with the substrate. Surface structure of the TiO_2-SiO_2 coating can be seen in **Figure 3** where SEM micrograph of its cross-section (right) and the corresponding EDS mapping (left) are shown. The composite layer keeps its structural characteristics, i.e., the same TiO_2 aggregates placed in SiO_2 matrix can be observed.

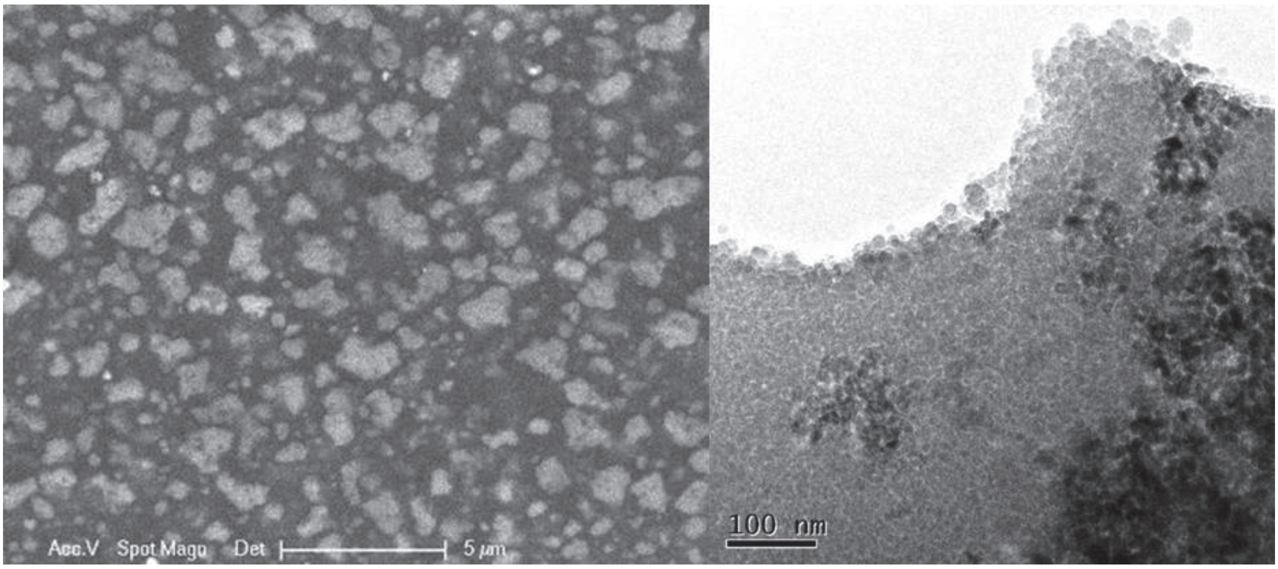

Figure 2 SEM (left) and TEM (right) micrograph of TiO_2-SiO_2 nanocomposite

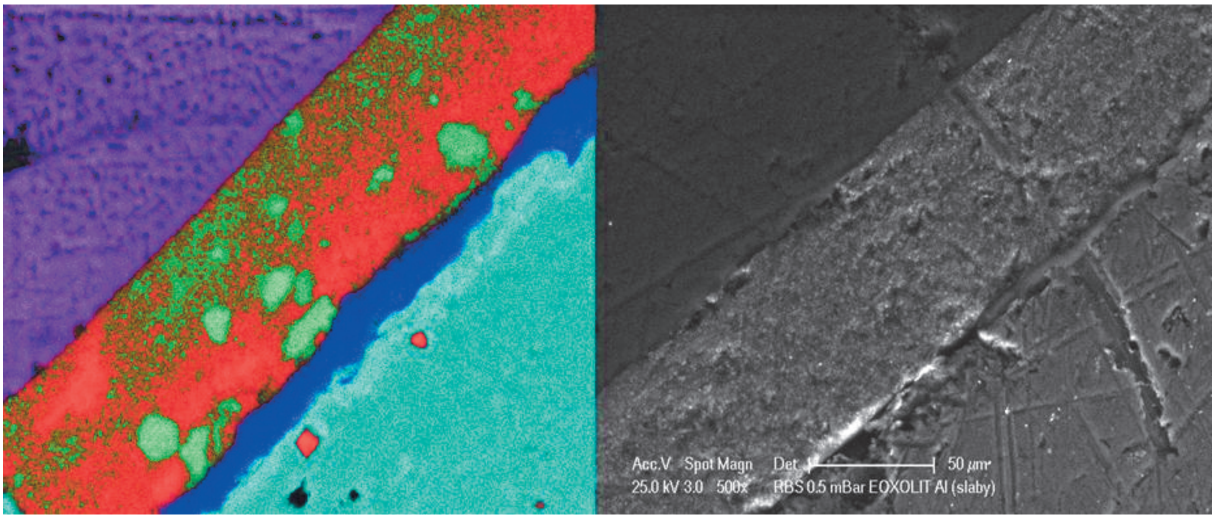

Figure 3 EDS mapping (left) and SEM micrograph (right) of cross-section of TiO_2-SiO_2 nanocomposite coating

3.2. Self-cleaning properties

The self-cleaning properties of the prepared TiO_2-SiO_2 nanocomposite coatings were characterized using the photocatalytic decolorization of methylene blue. The observed decrease of absorbance of aqueous solutions of methylene blue as a function of irradiation time for different supports is graphically illustrated in **Figure 4** (left). One can see that the TiO_2-SiO_2 coatings on all the used supports showed self-cleaning activity upon UVA irradiation. However, the observed self-cleaning activity depended on the substrate on which the nanocomposite was applied. The highest self-cleaning activity exhibited the coatings on silicate paint while the others support materials (lime plaster, acrylic and silicone paint) showed little reduced but similar self-cleaning activity.

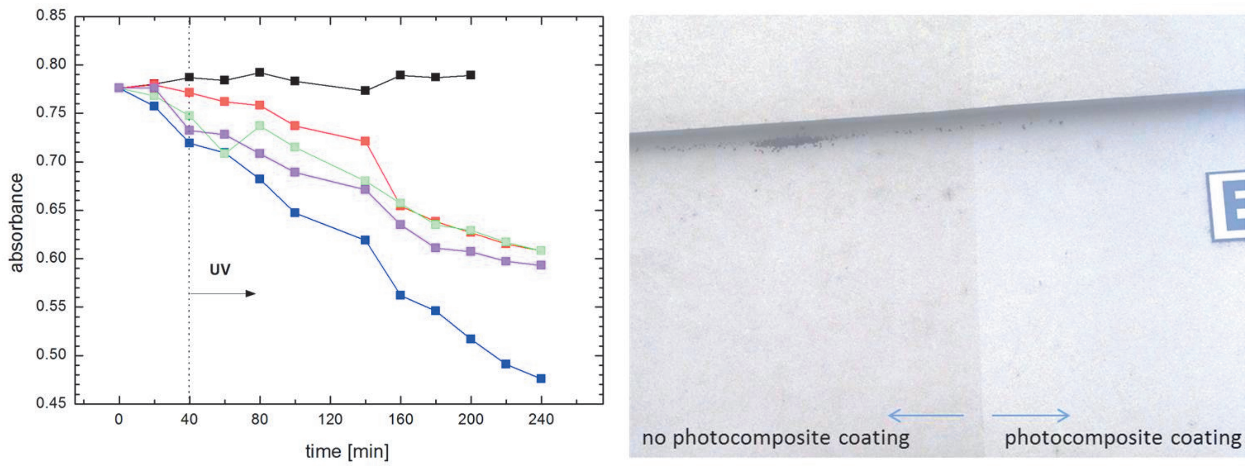

Figure 4 The course of photocatalytic degradation of methylene blue on TiO_2-SiO_2 nanocomposite coatings on **acrylic paint**, **silicone paint**, **lime plaster**, and **silicate paint** (left graph, **black** curve relates to blank experiment); photography of building facade comparing appearance of coated and non-coated places after 2 years of out-door exposition (right)

In addition to laboratory testing, the TiO_2-SiO_2 nanocomposite was also tested in real out-door conditions as a transparent coating of building facade. The photography in **Figure 4(right)** compares with coated and non-coated places. The picture was made two years after application of the TiO_2-SiO_2 nanocomposite coating.

The photocatalytic self-cleaning effect of the novel TiO_2-SiO_2 nanocomposite under real solar conditions is clearly evident. One can see visible difference between the dirty uncoated and clean coated parts of the originally white building facade.

3.3. Antimicrobial activity - algae degradation

Results of the antimicrobial activity of the TiO_2-SiO_2 nanocomposite coated on white marble and lime plaster are shown in **Figure 5**. The pictures were made after 24 hours of simulated sun light irradiation. Several stone pieces were always kept in each Petri dish, coated (left) and non-coated (right), to compare the photocatalytic effect on algae growth under identical conditions of the microclimate of particular Petri dish. It is obvious that the algae growth was totally suppressed on the substrates, which were coated with the TiO_2-SiO_2 nanocomposite (the algae growth on stones is labelled with white circles). However, if the TiO_2-SiO_2 nanocomposite was applied on the places with already expanded algae colonies no significant algae removal was observed. Additional experiments are in progress to investigate in detail the expected photocatalytic algicidal effect of the novel TiO_2-SiO_2 nanocomposite. However, the preliminary results already showed that this nanocomposite coating can be applied as prevention against algae growth.

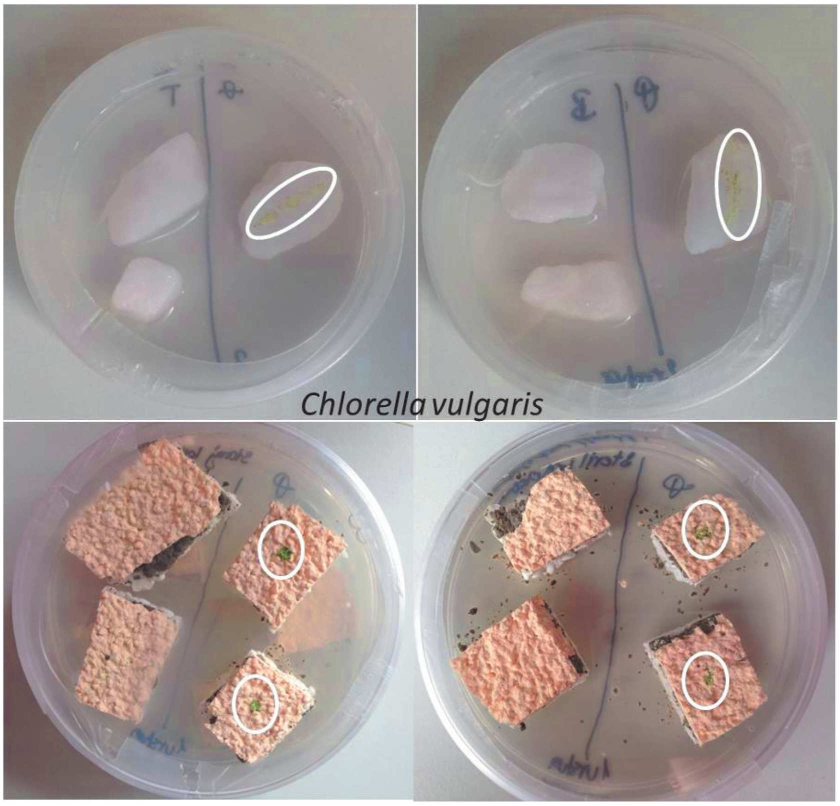

Figure 5 The algae growth testing on white marble (up) and on plaster (down). The samples on the right (left) part of petri dishes are not coated (coated) with TiO_2-SiO_2 nanocomposite. The algae are marked by a white circle

4. CONCLUSION

The applied SiO_2-TiO_2 nanocomposites consist of small aggregates of TiO_2 photocatalyst separated in matrix of SiO_2 nanoparticles. Such structure reduces further agglomeration of TiO_2 particles and prevents direct contact of the TiO_2 photocatalyst with the substrate on which he coating was applied. The prepared nanocomposite layers are transparent and represent an ecological and non-invasive way how to keep nice appearance of buildings for a long time. It is due to their permanent photocatalytic activity causing self-cleaning and algicidal effects. Such coatings may significantly reduce ageing processes on facades of buildings that are caused by microbiological pollution and smog exhalations.

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