

Application of semiconductor photocatalysis for surface disinfection and air purification

Využití polovodičové fotokatalýzy pro dezinfekci povrchů a čištění vzduchu

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Summary

Semiconductor photocatalysis represents a promising method to decompose organic pollutants dispersed in air or in aqueous phase (e.g. VOC, traces of herbicides, drugs, hormones etc). The other main application is based on so called self - cleaning ability - the combination of photogeneration of reactive species with oxidation potential and superhydrophilic properties. Superhydrophilic means that water doesn't form droplets on a surface coated with nanoparticulate TiO_2 which is irradiated by UVA light. What happens is that the contact angle decreases and created a water film on the surface. Such surface (typically building facade) is not to susceptible to soiling and thus this phenomenon help to keep the surface of buildings clean.

This contribution introduces the basic principles of photocatalysis and showcases applications in the two major domains of its commercial utilization – self-cleaning ability and air purification

Key words: TiO_2 , photocataytic activity, self – cleaning, paints, air purifiers.

Introduction

Photocatalytic activity is based on the ability of a photocatalyst to adsorbed quantum of energy higher than the band gap energy of given photocatalyst. Bandgap is the energy difference between the conductive and valence band of the photocatalyst. The most studied and applied photocatalyst is titanium dioxide of anatase modification. Titanium dioxide is the most widespread white pigment. Rutile modification is usually used in exterior paints due to the low photocatalytic activity and high refractive index. Anatase is often used in interior paints where the significant resistance against weathering is not expected. [1] Titanium dioxide is produced by a sulphate process in which ilmenite (FeTiO_3) reacts with sulphuric acid to form TiOSO_4 and FeSO_4 . After FeSO_4 removal, it is possible to get both anatase or rutile TiO_2 . Another technology is based on a reaction of titanium ore with chlorine in the presence of coke to form TiCl_4 which is then oxidized to get TiO_2 . Using chloride process it is possible to get rutile form of TiO_2 . [2]

As a benchmark is often in literature listed commercial photocatalyst TiO_2 material called Aeroxide P25 (produced by Evonik company). This material is produced by flame hydrolysis of titanium tetrachloride and it contains according to XRD about 70% of anatase and 30% of rutile, with anatase

crystalline size about 22 nm and specific surface area about 45 m²/g [3]. Than band gap energy of anatase is 3.2 eV, thus it follows that for excitation of electrons a photon must have a minimal wavelength 388 nm. Current research is therefore focused on sensitization of TiO₂ for visible light i.e. lowering the band gap energy [4].

Self - cleaning ability

Self - cleaning ability is based on combination of i) photocatalytic activity (production of reactive species with high oxidation potential which are able to decomposed organics compounds) and ii) superhydrophilic function properties. Superhydrophilic effect is explained in literature by absorption with water molecules of oxygen vacancies, which are created on photoirradiated TiO₂ surface. Titanium is then reduced by excited electrons to Ti³⁺, while the holes are oxidized the bridge oxygen atoms. In this process oxygen is released from the surface and oxygen vacancies are formed. Water molecules are then adsorbed on the surface creating hydrophilic properties.

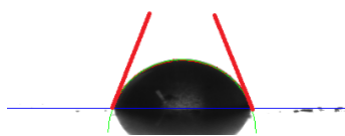


Fig. 1: Photocatalytic surface before UV irradiation

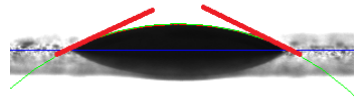


Fig. 2: Photocatalytic surface after UV irradiation

Self- cleaning ability can be applied in facade paints which are prepared with the aim to help to exterior of buildings clean. Overall it is important to find a compromise between reasonable photocatalytic activity and resistance against weathering. Organic binder can be decomposed by photooxidative reaction causing the chalking of the paint.

Commercial usage of self – cleaning paints involve the necessity of testing their photocatalytic efficiency. In a paper written by Mills [5], we can found various ISO methods suitable to determine the efficiency in gaseous phase ISO 22197-1 to ISO 22197-4 and also methods which can be used to determined self-cleaning properties. Suitable method which can be apply on self- cleaning paints is based on reduction of resazurin ink in the presence of glycerol which acts as a sacrificial electron donor. Photoinduced holes oxidize glycerol to glyceraldehyde or glyceryl acid while excited electrons reduce

resazurin to form of resorufin. This reduction is connected with a color change from blue to pink. This method can be utilized also outside do laboratory to qualified photocatalytic performance to determine if the studied surface exhibit photocatalytic activity. It is now also ISO method.

Using hand held scanner it is possible to recorded surface of photocatalytic samples painted with Resazurin ink. By software analysis of captured images to RGB color system it is possible to expressed normalized R channel as a function of irradiation time. Photocatalytic activity can be than expressed as time in which 90% of color changes occurs ($T_{tb\ 90}$ value (time to bleach) (Fig. 5).



Fig.3: Degradation of organic binder during weathering in QUV panel



Fig.4: Comparison of self- cleaning paint (left) and conventional paint (right) in atmospheric conditions

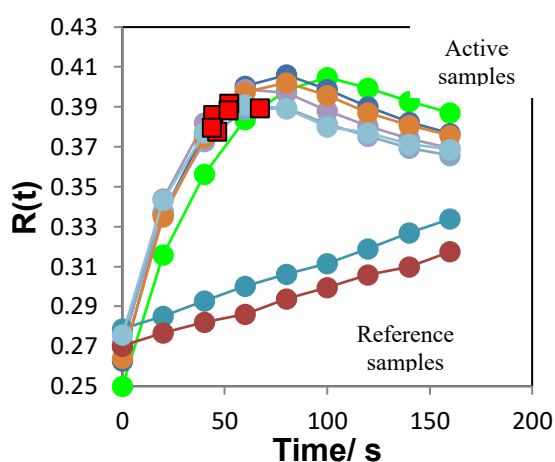


Fig. 5: Normalized red channel as a function of irradiation time. Ttb value expressed by red squares

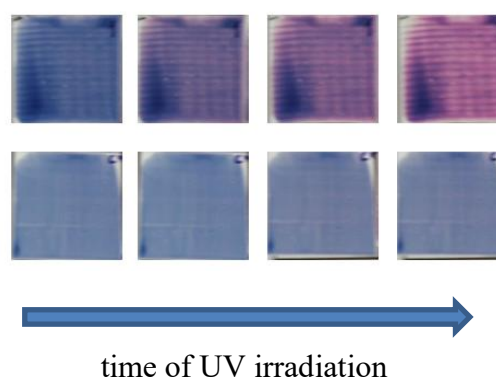


Fig. 6: Photocatalytic paint (up) and reference paint (bottom) with Resazurin film recorded on various exposition time

Air purification

Another practical application of semiconductor photocatalysis could be found in air treatment, where photocatalyst is applied to decompose traces of VOC or NO_x. Typical application could be in photocatalytic air purifiers which can decompose relatively low concentration of pollutants causing sick building syndrome. These pollutants are in high concentrations in new buildings as they slowly emerge from various varnishes and polymers. Typical example is acetaldehyde or formaldehyde which can be released from furniture causing in the long term exposition number of non-specific symptoms like nausea, headache. Photocatalytic purifiers can help with this problem as pollutants are oxidized to CO₂. Photocatalytic activity of such devices can be determined in 1m³ chamber by degradation of mixture of 4 VOC's namely acetaldehyde, acetone, heptane and toluene. This method is part of standard EN 168461. Tested air purifier is added to the testing chamber. Then appropriate volume of liquid pollutants are introduced to the chamber using a Hamilton syringe. The concentration of pollutants is measured under dark conditions to access potential adsorption of VOC by the device. Simultaneously the concentration of CO₂ is measured. After switching the tested device on the concentration of 4 compounds decreases while the amount of CO₂ produced increases. This allows to calculate the level of mineralization, i.e. the benefit of using such a device.

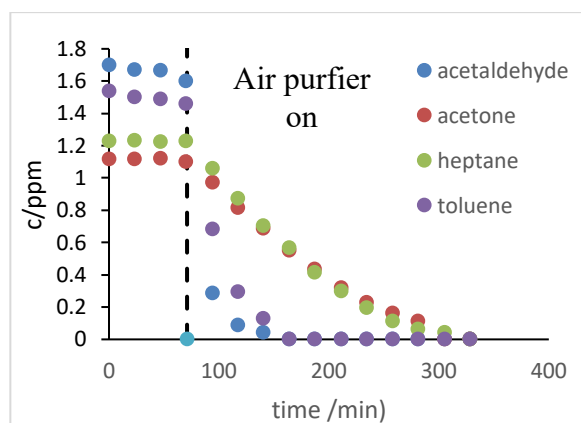


Fig 7: Concentration decay of 4 VOC during the during operation of the purifier

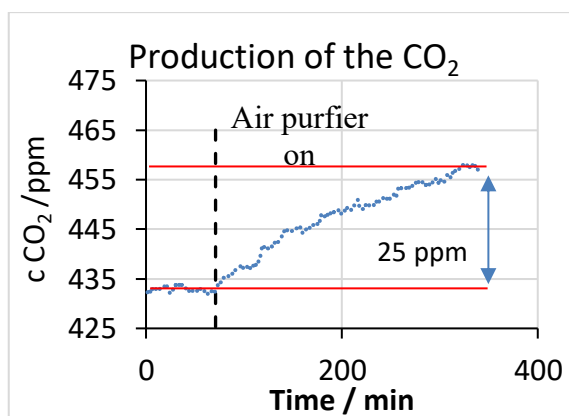


Fig. 8: Production of CO₂ during the operation of the purifier

Fig. 7 shows concentration of 4 VOCs depending on time of operation of air purifier. In the dark period the concentration of 4 VOCs is almost stable as well as the concentration of CO₂. After switching the device on concentration of VOCs decreases, while the amount of CO₂ increases. Theoretical amount of CO₂ produced by mineralization of the initial concentration of 4 VOCs is 26 ppm. This is in good agreement with measured value which indicates 25 ppm increase. It can be concluded that tested device is able to decompose VOC to CO₂ without forming significant amount of by products.

Conclusions

This contribution deals with practical application of photocatalysis on titanium dioxide – self cleaning surfaces and air purification. Beside practical application this paper also includes standards methods of testing that we routinely provide as a service at our institute which can be offered to our industrial partners.

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