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OA	Benedix, R., Dehn, F., Quaas,J., Orgass, M., „Application of Titanium Dioxide Photocatalysis to Create Self-Cleaning Building Materials", *LACER - Leipzig Annual Civil Engineering Report*, No.5, pp.157-168, 2000. Disponibil la: www . nanoes . com.

Incidența minimă a suspiciunii / Minimum incidence of suspicion	
p.280:05 – p.285:42	p.157:07 – p.167:12

Application of Titanium Dioxide Photocatalysis to Create Self-Cleaning Building Materials

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SUMMARY

To realize self-cleaning material surfaces there are two principal ways: the development of super-hydrophobic or super-hydrophilic materials. By transferring the microstructure of selected plant surfaces to practical materials like tiles and facade paints, super-hydrophobic surfaces were obtained (Lotus effect). Super-hydrophilic materials were developed by coating glass, ceramic tiles or plastics with the semiconducting photocatalyst titanium dioxide (TiO_2). If TiO_2 is illuminated by light, grease, dirt and organic contaminants are decomposed and can easily be swept away by water (rain). Subject of our further research is a detailed study of the interaction between TiO_2 and traditional building materials like concrete, mortar and plaster.

1 INTRODUCTION

In practice, surface cleaning of building materials like tiles, facades and glass panes causes considerable trouble, high consumption of energy and chemical detergents and, consequently, high costs. To realize self-cleaning material surfaces there are two principal ways: the development of so-called super-hydrophobic or super-hydrophilic surfaces.

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The wetting of a solid with water, where air is the surrounding medium, is dependent on the relation between the interfacial tensions (water/air, water/solid and solid/air). The ratio between these tensions determines the contact angle θ between a water droplet on a given surface. A contact angle of 0^o means complete wetting, and a contact angle of 180^o corresponds to complete non-wetting.

Hydrophobic surfaces with low wettability and contact angles of about 100^o are known for a long time. The higher this angle the lower is the value of the adhesion work. Decreasing of the contact angle leads to enlarged values of the adhesion work (hydrophilic surfaces).

By transferring the microstructure of selected plant surfaces to practical materials, *super-hydrophobic* surfaces could be developed. The water repellency of plant surfaces has been known for many years. That water-repellent surfaces also indicate self-cleaning properties has been completely overlooked. Recently, Barthlott et al. [1] investigated and proved the correlation between the microstructure, wettability and contaminants in detail using lotus leaves. This was called the *Lotus Effect* because it can be demonstrated beautifully with the great leaves of the lotus plant. The microrough surfaces show contact angles higher than 130^o. That means, the adhesion of water, as well as particles is extremely reduced. Water which contacts such surfaces will be immediately contracted to droplets. The particles of contaminants adhere to the droplet surfaces and are removed from the rough surface when the droplets roll of (fig. 1).

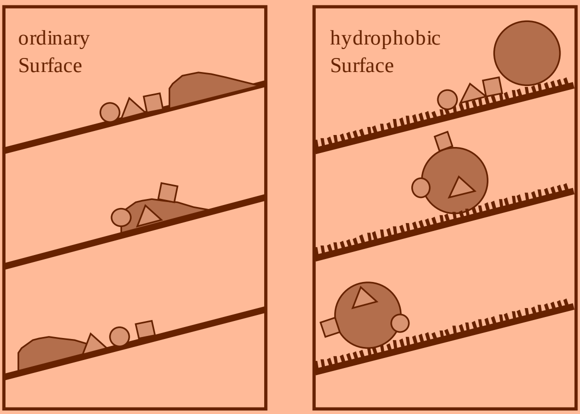

Fig. 1: Lotus Effect

Cleaning procedures based on low contact angles are known since the discovery of soap (3rd millennium BC). Generally, detergents reduce the surface tension of water and the contact angle will lowered. Another very interesting possibility to cause low contact angles without detergents is the use of active thin films on the material surface. For the preparation of this thin layers mainly photocatalytic active metal oxides or sulfides have been applied. In the last years TiO_2 coated materials are of increasing interest [2]. If TiO_2 of the anatase type is exposed to UV light very low contact angles are obtained ($< 1^o$). These materials have the unique property of "attracting" rather than repelling water *(super-hydrophilicity)*. The water lies flat on the surface in sheets instead of forming droplets. If the illumination is stopped, the super-hydrophilic behaviour of the TiO_2 surface is retained for approximately two days. Furthermore, UV illumination of titanium dioxide leads to the formation of powerful agents with the ability to oxidize and decompose many types of bacteria, organic and inorganic materials. In the following, the principles and potential applications of TiO_2 photocatalysis are discussed.

2 BASIC PRINCIPLES OF HETEROGENEOUS PHOTOCATALYSIS

In absence of a catalytic active substance, the oxidation of the most hydrocarbons proceeds rather slowly, which can be explained by kinetic arguments. A photocatalyst decreases the activation energy of a given reaction. In the result of photoinduced processes often particles with strong oxidation and reduction ability occur.

A heterogeneous photocatalytic system consists of semiconductor particles (photocatalyst) which are in close contact with a liquid or gaseous reaction medium. Exposing the catalyst to light excited states are generated which are able to initiate subsequent processes like redox reactions and molecular transformations.

In fig. 2 a simplified reaction scheme of photocatalysis is shown. Due to their electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB), semiconductors (metal oxides or sulfides as ZnO, CdS, TiO_2, Fe_2O_3, and ZnS) can act as sensitizers for light-induced redox processes. The energy difference between the lowest energy level of the CB and the highest energy level of the VB is the so-called band gap energy E_g. It corresponds to the minimum energy of light required to make the material electrically conductive.

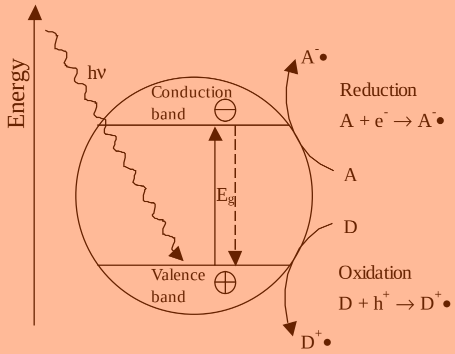

Fig. 2: Operation of a photochemical excited TiO_2 particle

When a photon with an energy of hν exceeds the energy of the band gap an electron (e^-) is promoted from the valence band to the conduction band leaving a hole (h^+) behind. In electrically conducting materials, i.e. metals, the produced charge-carriers are immediately recombined. In semiconductors a portion of this photo-excited electron-hole pairs diffuse to the surface of the catalytic particle (electron-hole pairs are trapped at the surface) and take part in the chemical reaction with the adsorbed donor (D) or acceptor (A) molecules. The holes can oxidize donor molecules (1) whereas the conduction band electrons can reduce appropriate electron acceptor molecules (2).

$$D + h^+ \rightarrow D\bullet^+ \quad (1)$$

$$A + e^- \rightarrow A\bullet^- \quad (2)$$

A characteristic feature of semiconducting metal oxides is the strong oxidation power of their holes h^+. They can react in an one-electron oxidation step with water (3) to produce the highly reactive hydroxyl radical (•OH). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic contaminants.

$$H_2O + h^+ \rightarrow \bullet OH + H^+ \quad (3)$$

In general, air oxygen acts as electron acceptor (4) by forming the super-oxide ion $O_2\bullet^-$.

$$O_2 + e^- \rightarrow O_2\bullet^- \quad (4)$$

Super-oxide ions are also highly reactive particles, which are able to oxidize organic materials.

3 TiO_2 AS PHOTOCATALYST

Titanium dioxide is one of the basic materials in everyday life. It has been widely used as white pigment in paints, cosmetics and foodstuffs. TiO_2 exists in three crystalline modifications: rutile, anatase, and brookite. Generally, titanium dioxide is a semiconducting material which can be chemically activated by light. The photoactivity of TiO_2 which is known for approx. 60 years is investigated extensively. For a long time there was a considerable problem especially what its application as pigment concerns. Under the influence of light the material tends to decompose organic materials. This effect leads to the well-known phenomenon of ”paint chalking”, where the organic components of the paint are decomposed as result of photocatalytic processes.

Compared with rutile and brookite, anatase shows the highest photoactivity. Therefore, the TiO_2 used in industrial products is almost exclusively from the rutile type. In the following, TiO_2 always denotes the anatase modification.

In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes [3]. This event marked the beginning of a new era in heterogeneous photocatalysis. Although TiO_2 absorbs only approx. 5 % of the solar light reaching the surface of the earth, it is the best investigated semiconductor in the field of chemical conversion and storage of solar energy. In recent years semiconductor photocatalysis using TiO_2 has been applied to important problems of environmental interest like detoxification of water and of air.

TiO_2 is a semiconductor with a band gap energy E_g = 3,2 eV. If this material is irradiated with photons of the energy > 3,2 eV (wavelength λ < 388 nm), the band gap is exceeded and an electron is promoted from the valence to the conduction band. Consequently, the primary process is the charge-carrier generation (5).

$$TiO_2 + h\nu \rightarrow h^+ + e^-\qquad (5)$$

The ability of a semiconductor to undergo photoinduced electron transfer to adsorbed particles is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbates. The relevant potential level of the acceptor species is thermodynamically required to be below the conduction band of the semiconductor. Otherwise, the potential level of the donor is required to be above the valence band position of the semiconductor in order to donate an electron to the empty hole. The band-edge positions of several semiconductors are presented in fig. 3.

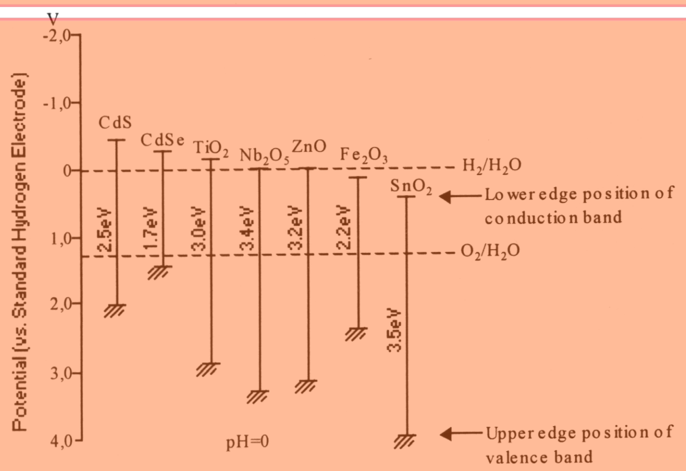

Fig. 3: Band-edge energies of typical semiconductors

The heterogeneous photocatalytic oxidation with TiO_2 meets the following requirements what could make it competitive with respect to other processes oxidizing contaminants:

- A low-cost material is used as photocatalyst.
- The reaction is quite fast at mild operating conditions (room temperature, atmospheric pressure).
- A wide spectrum of organic contaminants can be converted to water and CO_2.
- No chemical reactants must be used and no side reactions are produced.

4 PRACTICAL APPLICATIONS OF TiO_2 PHOTOCATALYSIS

In fig. 4 the main areas of activity in titanium dioxide photocatalysis are shown. As already mentioned, in the last 10 years photocatalysis has become more and more attractive for the industry regarding the development of technologies for purification of water and air. Compared with traditional advanced oxidation processes the technology of photocatalysis is known to have some advantages, such as ease of setup and operation at ambient temperatures, no need for postprocesses, low consumption of energy and consequently low costs.

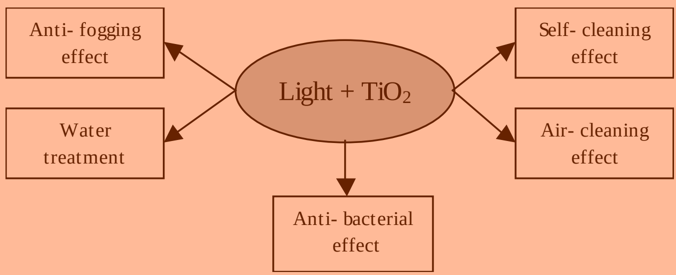

Fig. 4: Major areas of activity in titanium dioxide photocatalysis

In the field of waste water detoxification numerous concepts were created [4; 5]. In previous studies, systems are considered in which the fine TiO_2 photocatalyst powder was dispersed in liquid suspension. However, these systems were hardly to handle. After the degradation process under irradiation with UV light the powder remains suspended in water. The use of filters or other methods to remove TiO_2 has been proved to be inefficient and cost-effective. In the following time, reactors were designed where the titanium dioxide is fixed on a glass, ceramics or metal surface. Presently there is high interest in development and improvement of thin-film-fixed-bed reactors, which is shown in fig. 5. In this reactor type industrial waste water is passing a TiO_2 coated material (glass, polystyrene, methacrylate).

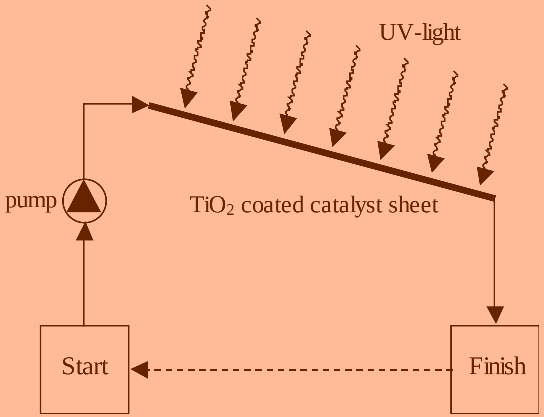

Fig. 5: Thin-film-fixed-bed reactor [5]

Photocatalytic oxidation has been applied for removing and decomposing pollutants in indoor air. The used reactors trap and chemically oxidize organic compounds, converting them primarily to CO_2 and water. These reactors operate at room temperature and with negligible pressure. Therefore, they may be readily integrated into new and existing heating, ventilation, and air conditioning systems.

TiO_2 coated ceramic tiles are considered to be very effective against organic and inorganic materials, as well as against bacteria. In fig. 6 Hydrotect® tiles are shown which kill bacteria at an extremely high rate of speed [6]. With other words, the bacteria are killed faster than they can grow. The application of these tiles in hospitals and care facilities to reduce the spread of infections and the threat to patients whose immune system have been weakened, in public and commercial facilities and schools to improve the hygienic conditions and in residential kitchens, baths and floors to promote family hygiene and to reduce housework is of general interest. Furthermore, these tiles show super-hydrophilic behaviour. Water forms a uniform sheet over the surface at a contact angle of 7 (exterior) and 25 (interior) degrees. Grease, dirt and other staining materials can easily be swept away with a stream of water. Superhydrophilicity, combined with the strong photocatalytic oxidizing properties makes this tile self-cleaning in exterior applications.

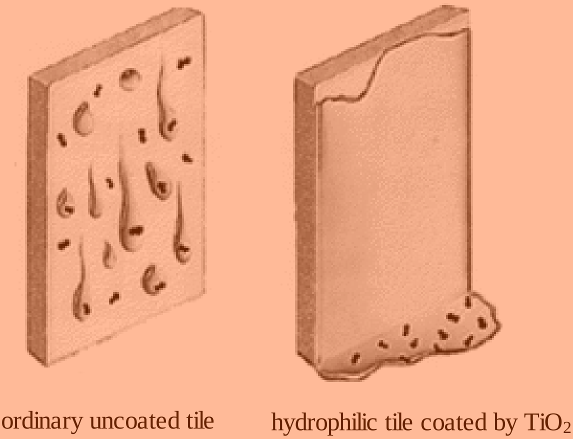

Fig. 6: Super-hydrophilicity

5 FURTHER INVESTIGATIONS

Although there are outdoor applications of TiO_2 photocatalysis, in the literature no information on the interaction between titanium dioxide and traditional building materials like concrete, mortar, and plaster is available as yet. For example, most of the external building walls become spoiled from automobile exhaust gases, which contain oily components. By coating the original building materials with a super-hydrophilic photocatalyst, the dirt of the walls can easily be washed away by rain, keeping the building external wall clean for long times. Two effects should be considered: Firstly, a super-hydrophilic surface has a higher affinity to water than to oil. Secondly, ultraviolet illumination of TiO_2 leads to the formation of a photogenerated hole-electron pair that reacts with oxygen and water in the environment to generate potential cleaning agents on the surface of the coated material. The agents (•OH, •OOH) decompose large organic molecules to smaller fragments. The combination of photocatalysis and super-hydrophilicity allows grease and dirt to be swept away with water.

Subject of our research is the detailed investigation of the dependence of the photocatalytic activity of TiO_2 on different building materials. The following items should be investigated:

- Possibilities of fixing TiO_2 on building materials
  - Application of the spray-coating technology
    The aqueous or methanolic TiO_2 suspension is sprayed on the surface of the considered building material. This method has the advantage that the amount of TiO_2 which shall cover a specific area of the sample can be regulated in a simple way. After spraying, the solvent can be removed by heating the sample to approx. 100° C.
  - Application of the sedimentation technology
    The sample is kept for a defined time in a TiO_2 suspension. Then the suspension slowly is drained from the beaker. Again, the solvent can be removed by heating the sample to approx. 100° C.
- The photocatalytic decomposition of organic dyes (methylene blue, rhodamine B, and others) as model substances for organic contaminants
- The photocatalytic decomposition of grease and varnish
- Time-dependent measurements of the decomposition reactions

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