

KRONOClean – Cleaning with light

Visible light photocatalysts based on titanium dioxide and their potential applications - An introduction by Dr. Stephan Blöß

Titanium dioxide is a well-known UV-absorber but it can also be used for initiating chemical reactions by ultra-violet radiation. By doping this semiconductor with carbon, interstate energy levels between the energy bands are formed. This offers the possibility not only to use ultraviolet radiation, but also visible light to activate the catalyst. In a cyclic photocatalytic process inorganic radicals are generated from the surrounding atmospheric water and oxygen. These radicals then oxidize organic compounds e.g. aromatic and aliphatic hydrocarbons or inorganic molecules e.g. nitrogen oxides and carbon monoxide, respectively, to carbon dioxide, nitrates and water as end-products, which can readily be assimilated by vegetation. Potential applications of these photocatalysts are found in self-cleaning surfaces and the reduction of air and water pollution, where its super-hydrophilicity and high specific surface areas can be utilized.

1. Introduction

Titanium dioxide (TiO_2) has been used as a pure white pigment since nearly a century now. Due to its high refractive index, numerous matrices can be pigmented with TiO_2 resulting in substrates having a good hiding power [1]. The well known semiconductor properties of TiO_2 with a band gap of 3.2 eV for the anatase modification and 3.0 eV for the rutile modification which relates to a cut-off wavelength of 388 nm and 413 nm, respectively, can be used to absorb UV-radiation. The absorption of this “aggressive” radiation can protect the substrate and hinders the de-gradation of the polymer matrix. Unfortunately, when TiO_2 absorbs UV-radiation, it generates radicals on the pigment surface, which in turn can damage the polymer molecules of the matrix [2]. In

order to prevent this process to happen, TiO_2 pigments are generally coated with various colourless metal oxides, like alumina, silica and zirconia.

Since the late 1970's, scientists started to investigate the useful side of the semiconductor properties of TiO_2 . Lab-scale investigations have shown that the radicals generated in the course of the photocatalytic process are able to degrade pollutants such as toxic gases or unpleasant odours [3]. The band gap of the semiconductor TiO_2 can be narrowed by doping the titanium dioxide with specific elements e.g. carbon or transition metals, for example iron. Depending on the type of dopant chosen, whether its nature is anionic or cationic or of the interstitial type, differences in the size of the band gap are observed [4]. The formation of interstate energy levels between the valence and the conduction band offers the possibility not only to use ultraviolet radiation, but also visible light for exciting a valence band electron. This exciton (electron-hole-pair) reacts with surface adsorbed water and oxygen molecules to form hydroxyl and perhydroxyl radicals. These radicals, in turn, can oxidize both organic and inorganic molecules. Consequently atmospheric pollutants can be degraded to eco-friendly derivatives and the level of contamination in water and on surfaces can be significantly reduced. To be effective the photocatalyst needs light (energy) and air (water and oxygen) and have a direct contact to the pollutant (a gas, liquid or solid). For most applications an immobilization of the catalyst on the surface of a matrix or embedding it in a porous structure, which is translucent for visible light is preferable.

The efficiency of such photocatalysts is evaluated by studying the rate of reduction of test substances such as nitrogen monoxide or acetaldehyde and comparing it to results measured with conventional photocatalysts for UV-radiation.

2. The electronic band structure

For conducting properties one has to differentiate between three different solid states: conductors (e.g. metals like gold and silver), insulators (e.g. polymers like Polypropylene and Polysiloxanes) and semiconductors (e.g. semi-metals like silicon and germanium) or semi-insulators (Fig 1). In a solid state the atomic orbitals of the elements are united to energy bands. Due to the fact that in a solid there are always more orbitals available than electrons, the electrons occupy the lower energy band called the valence band (VB). The higher energy band, which is unoccupied is called conduction band (CB). In conductors these bands are close to each other (band gap energy $E_g < 0.1$ eV) so that electrons can easily be excited by the energy of room temperature from the VB to the CB resulting in a measurable electrical current, which is known from metals (Fig 1a). For the insulator it is just the opposite. The two bands are far apart ($E_g > 4.0$ eV), so that electrons can not be excited from VB to CB (Fig 1c) by energy of moderate temperatures or middle wavelength radiation. The semiconductors or semi-insulators are situated in between these two extreme possibilities. The bands are separated (0.1 eV $< E_g < 4.0$ eV) but the energy of elevated temperatures or normal radiation is sufficient to excite an electron (e-) from the VB to the CB (Fig 1b). The resulting "lost-electron" is called hole (h+) and is mobile within the VB. The same is with the electron which can move within the CB. If the excitation energy originates from light radiation, the solid is called a photo-semiconductor. The radiation wavelength used to excite one electron in

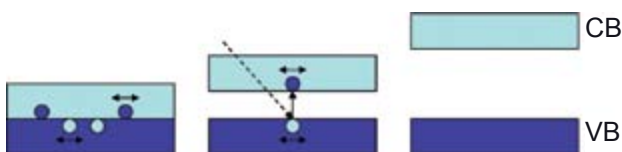


Fig 1: Valence band (VB) and conduction band (CB) of metal (a), semiconductor (b) and insulator (c)

the anatase modification of TiO_2 has to be below 388 nm (UV-A-light), in the rutile modification below 413 nm (dark violet light).

In addition to the specific properties of a solid, one can incorporate additional energy levels between the electron bands by doping it with selected elements. This dopant can either replace one of the matrix elements in the anionic (Fig 2a) or in the cationic sub lattice (Fig 2b) which consequently leads to distortions of the lattice.

These distortions result in changes inside the band structure in the form of interstate energy levels (Fig 3a) or deformation of the VB band itself (Fig 3b). Following the theory of exciting electrons by radiation, less energy is then required and the so called cut-off wavelength is shifted to higher values. By doping TiO_2 with carbon [5-8] in the cationic sub lattice, the cut-off wavelength of the anatase modification is shifted to 535 nm (bluish green light). Consequently only 2.32 eV has to be transferred into the system instead of 3.2 eV for the pure anatase.

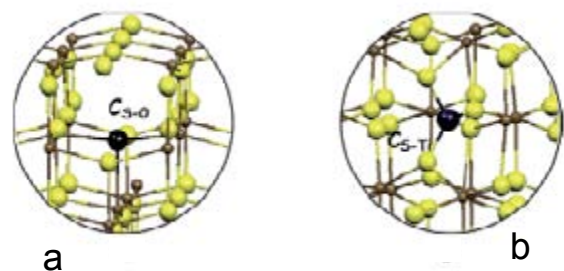


Fig 2: Carbon doped into the oxygen sub lattice (a) or the titanium sub lattice (b) [9]

3. Photocatalysis

Catalysis is defined as the acceleration of chemical reactions by certain substances (called catalysts) without these being consumed during the reaction. Generally catalysis takes place by reducing the activation energy, which means changing the kinetics

but not the thermodynamics of a chemical reaction. Important for a true catalytic reaction cycle is that the catalyst returns to the same state when the reaction has ended as it was at the beginning. One has to differentiate between homogenic and heterogenic catalysts. Homogenic catalysts are present in the same phase state as the reactants (e.g. liquid/solution), whereas heterogenic cata-

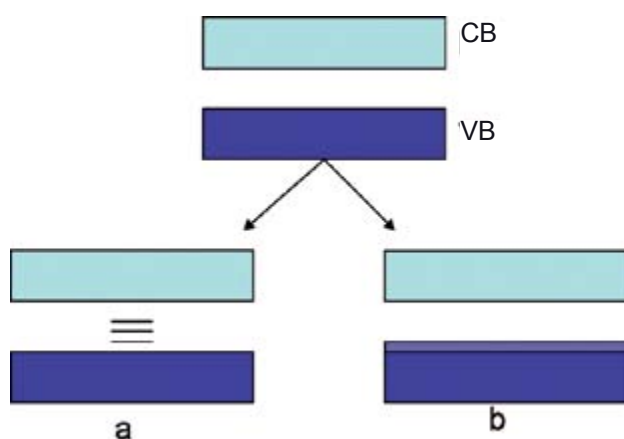


Fig 3: Gap changes via interstates (a) or expansion of the band (b)

lysts are present in another phase state (e.g. solid/liquid). Well known examples of homogenic catalysts are the Ziegler-Natta-catalysts for polymerisation and of heterogenic catalysts are the Raney-Nickel-catalysts for hydrogenation-reactions. In photocatalysis, following this definition, radiation or the particle form of an electromagnetic wave, a photon, can not be called a catalyst. This is because the energy of this photon is absorbed and used for the chemical reaction and no photon of the same state is emitted afterwards. To be more precise one has to call it a “photo-induced catalysis”. An example is the photo-synthesis of plants.

A semiconductor can also work as a photocatalyst by absorbing light energy and transforming this energy to chemical reactants. In the case of TiO_2 the mechanisms that takes place are well studied, because of the wide spread use of TiO_2 as a white

pigment in various applications. A matrix pigmented with untreated TiO_2 is destroyed gradually when it is exposed to sunlight. This effect is called chalking, because the white powder (pigment) can be rubbed off the degraded matrix surface (Fig 4).

The photocatalytic cycle behind this degradation of the polymer matrix starts with the absorption of light of a certain wavelength. This energy excites an electron from the VB into the CB (Fig 5 A). Within these bands, the generated electron-hole-pair can move to the crystal surface (Fig 5 B), where adsorbed water (H_2O) and oxygen (O_2) can be transformed into radicals (Fig 5 C). This reaction is split into two parts:

1. reduction of oxygen by the electron of the CB into a perhydroxyl radical (HO_2^\cdot) and
2. oxidation of water by the hole of the VB into a hydroxyl radical (HO^\cdot).

These radicals, which in nature are also formed during normal UV-radiation on atmospheric water in the stratosphere, can react with organic molecules (e.g. aromatic and aliphatic hydrocarbons) as well as not fully oxidised inorganic compounds (e.g. nitrogen oxides, carbon mo-noxide) in an oxidation process (Fig 5 D). The inorganic “pollutants” are mineralised up to their highest possible oxidation state (e.g. carbon monoxide (CO) reacts to carbon dioxide (CO_2) or carbonic acid (H_2CO_3 ; Fig 5 E).

4. Evaluating the photocatalytic effect

There are a number of possibilities to make the photocatalytic process visible. Electron spin resonance (ESR) measurements are able to detect single electrons via trap molecules. This is a method where the radicals can be detected directly. In a more indirect, but common method one can monitor the oxidation of test molecules. These measurements are very important for the determination of a whole oxidation process with all its intermediate products. Acetal-

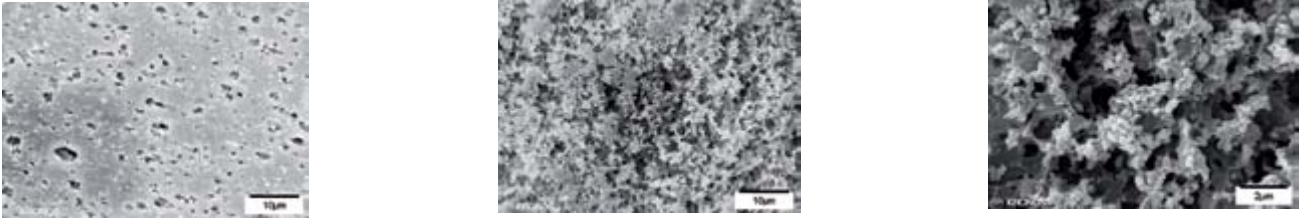


Fig 4: Pigmented PVC after exposure to Xe light (left: weakly destroyed; middle: chalking surface; right: magnification of middle)

dehyde and isopropanol are often used as test representatives for volatile organic compounds (VOC) as well as nitrogen monoxide or carbon monoxide as representatives of toxic inorganic gases. For measuring water based pollutants it is common to use easy to detect substances like dyes (methylene blue, resazurine or rhodamine) or chlorinated hydrocarbons (e.g. 4-Chlorophenole). A third method, but most time-consuming is the classical weathering of substrates containing the photocatalyst via accelerated weathering in QUV- or WOM-setups or normal outdoor weathering.

Except for ISO 22197-1 (2007) [10] no further standard measurement procedures for measuring photocatalysis are available. These will eventually be established within the next years by the international and national organisations for standardisation.

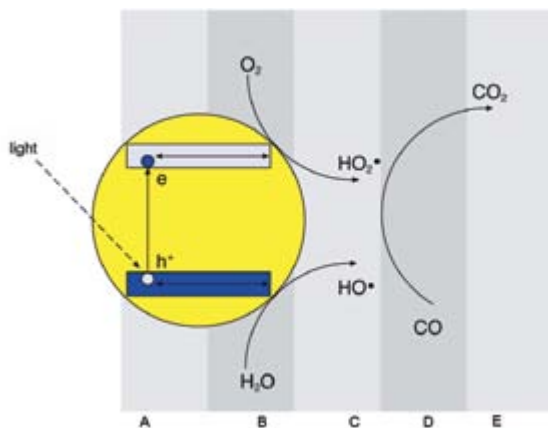


Fig 5: Mechanism of the photocatalytic process of TiO_2

Investigations with the visible light photocatalyst (carbon doped TiO_2), regarding the reduction of acetaldehyde, have been examined in detail. The infrared spectra of acetaldehyde and carbon dioxide are observed over a period of time (13 hours) in which the photocatalyst is irradiated with visible light (Fig 6). Analogue to the formal oxidation process of acetaldehyde, two moles of carbon dioxide are formed per mole of acetaldehyde which results in a twice as high increase rate of the CO_2 signal relative to the decline rate of the aldehyde signal.

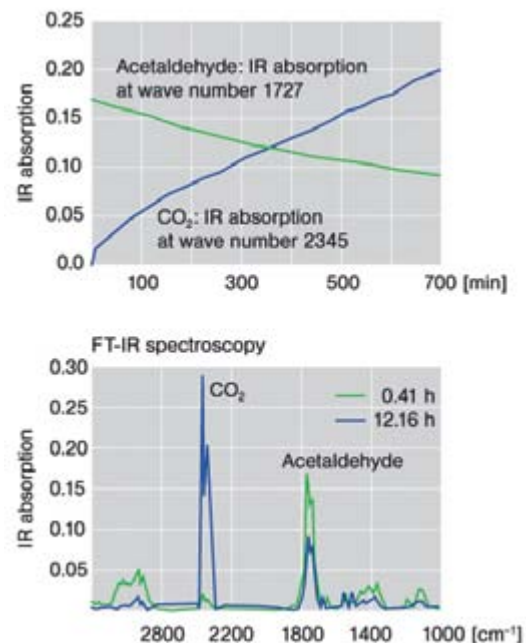


Fig 6: Decomposition of acetaldehyde by visible light photocatalyst titanium dioxide

5. Potential applications of TiO₂ photocatalysts

For pure TiO₂ surfaces the adsorbed water and oxygen molecules together with the generated oxygen containing radicals result in a high concentration of polar groups, which lead to an effect called super-hydrophilicity. This means that the contact angle between the surface and a water droplet is less than 5°. Due to this fact, the water does not remain as a droplet but spreads into a thin film. One of the self-cleaning mechanisms of surfaces is found in this anti-fogging effect and is completely the opposite to super-hydrophobicity of fluorosiloxanes or the so called Lotus-effect. In the latter case, a water droplet picks up the dust off the surface, which is then spread into a thin layer over the surface of the droplet. If such a dust loaded droplet dries on the surface, the small dust particles are concentrated at the interface to the surface. These will remain as a dust-ring, which can be seen by the human eye (Fig 7a). In case of untreated surfaces the polarity will result in a more or less hydrophobic situation, where dust is partly washed away, but drying droplets result in typical tear drop traces of dust (Fig 7b). In the case of the super-hydrophilic surface, the drying of the dust loaded water film will result into a uniform layer of dust particles, which are hardly to be visible by eye (Fig 7c). This self-cleaning property is already used on glass surfaces for windows, mirrors and ceramic tiles. In addition to this effect the photocatalytic process supports the cleaning effect by oxidising the adhesive pollutants into volatile carbon dioxide.

Due to the fact, that the photocatalytic process takes place on the interface between the TiO₂ and its surrounding, it is advantageous to generate as much catalytic surface as possible which is the case for nanoscale particles.

One of the most used parameters to specify catalysts is the specific surface area, often measured by gas adsorption (BET method). This high surface area of the catalyst should be retained in its final application (e.g. rough surfaces of ceramics). In order to keep the photocatalytic cycle going, TiO₂ needs direct contact to air (water in form of humidity and oxygen) as well as to the pollutant and has to be under the radiation of light. For most applications an immobilisation on a substrate is favourable but not absolutely necessary.

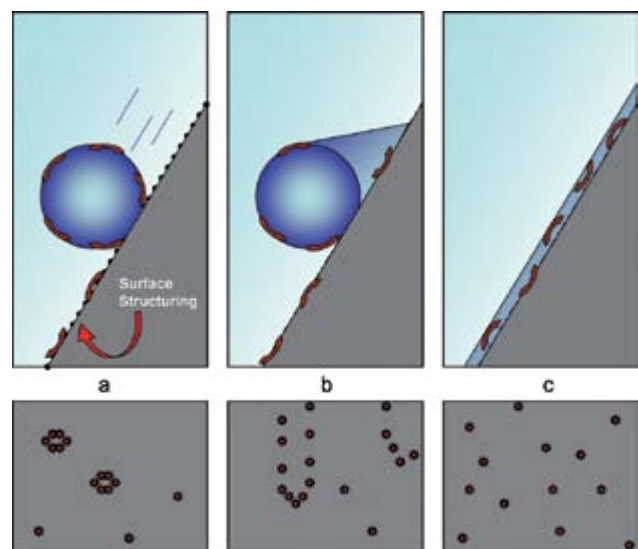


Fig 7: Super-hydrophobicity (a), hydrophobicity (b) and super-hydrophilicity (c) of surfaces

6. Conclusion

The semiconducting properties of titanium dioxide can be modified by doping them with non-metals as well as transition metals. Doping the anatase modification with carbon into the cationic sub lattice adds some additional interstate energy levels in the band gap model. This expands the scope of usage of the photocatalytic process from the UV- into the visible light region. The photocatalytically generated radicals are able to oxidise atmospheric pollutants to their highest oxidation state, which is generally carbon dioxide, water and nitrate. This purification effect can be used for decontaminating air and water with light. Through the superhydrophilic property of titanium dioxide the surface can be self-cleaning without being mechanically instable as it is with surfaces using the Lotus-effect.

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First published in: Tenside Surfactants Detergents, 44 (2007) 5 Carl Hanser Publisher, Munich, Germany.