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Photocatalytic activity of TiO_2

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1 Introduction

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium with chemical formula TiO_2 . It is also known as a pigment (very bright with very high refractive index i.e. $n=2.7$) called titanium white, Pigment White 6 or CI 77891 and as food colouring E171. This oxide is widely used and studied due to its properties (see section 2). My recent research is concerning TiO_2 as a photocatalyst.

The superhydrophilicity phenomenon of glass coated with TiO_2 and exposed to sun light was discovered in 1995. TiO_2 incorporated into outdoor building materials and paints reduces concentrations of airborne pollutants. Even more, using photocatalysis, there is no need to use conventional cleaning chemicals i.e. there is no extra pollution using photocatalytical effect. Result of this knowledge was development of self-cleaning glass and anti-fogging coatings. Photocatalytical effect of TiO_2 can be also used in wastewater detoxification[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15].

TiO_2 can nowadays be used in medicine. It allows osseointegration between an artificial medical implant and bone. Before implanting photocatalytical effect can be used to annihilate the bacteria on surface. TiO_2 was recently incorporated as a photocatalyst into dental bleaching products. It allows the use of decreased concentrations of hydrogen peroxide in the bleaching agent achieving similar bleaching effects with less side effects.

TiO_2 on SiO_2 is being developed as a form of odour control in cat litter. This photocatalyst is cheaper than the purchased SiO_2 beads and more effective in odour-eliminating process.

TiO_2 is nowadays used in different applications. Many of them use the fact, that TiO_2 is a n-type semiconductor.

2 Properties of TiO_2 Nanomaterials

2.1 Structural Properties

Titanium dioxide occurs in nature as three different minerals: rutile, anatase and brookite. The most common form is rutile, which is also the most stable form. Anatase and brookite both convert to rutile upon heating. Brookite is in nature the least common between all of them.

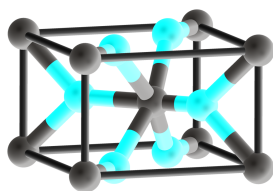


Figure 1: Crystal structure of rutile TiO_2 [16].

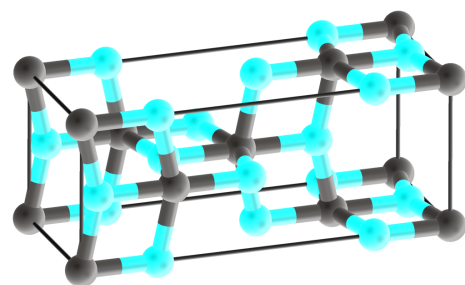
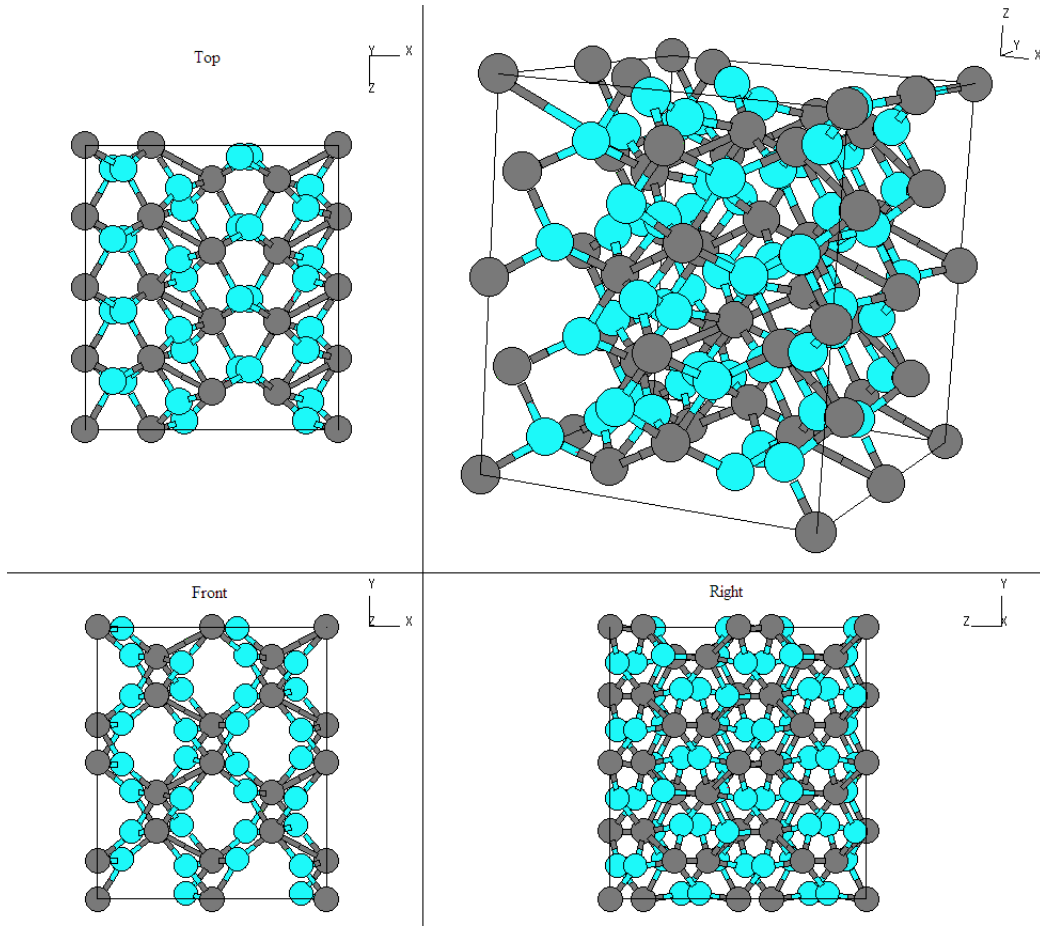


Figure 2: Crystal structure of anatase TiO_2 [16].

Figure 3: Crystal structure of brookite TiO_2 [17].

Rutile and anatase crystallize in the tetragonal system. On the other hand brookite crystallizes in the orthorhombic system and shows no photocatalytic activity.

The Ti-Ti distances in anatase are larger, the Ti-O distances are shorter comparing to rutile. In the rutile, each octahedron is in contact with 10 octahedrons, in the anatase with 8. The result in differences in structures of anatase and rutile is different mass density and different electronic band structures [18].

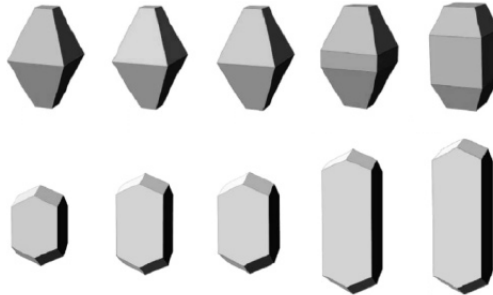


Figure 4: Morphology of anatase (top) and rutile (bottom) grown in different environments[18].

2.2 Thermodynamic Properties

Rutile represents the stable phase of TiO_2 at high temperatures. On the other hand anatase and brookite are common in nanoscale grained samples. When heating different transformations can occur: anatase→brookite→rutile, brookite→anatase→rutile, anatase→rutile, brookite→rutile. Which transformation will occur depends on initial particle size. Still, inconsistent results were observed. However, observed was

- for particles smaller than 50 nm, anatase is more stable and transforms to rutile at higher temperature than 973 K (*Hwu*).
- nanoparticles of anatase and/or brookite transform into rutile after reaching certain size. Rutile becomes more stable than anatase when particles are bigger than 14 nm (*Banfield*).
- - slow brookite→anatase transition below 1053 K along with grain growth (*Ye*).
 - rapid brookite→anatase→rutile transition between 1053 K and 1123 K (*Ye*).
 - rapid grain growth of rutile above 1123 K (*Ye*).
 - nanocrystals of brookite→rutile above 973 K (*Kominami*).
- for equally sized nanoparticles, anatase is thermodynamically stable for sizes below 11 nm, brookite is stable for sizes between 11 and 35 nm, rutile is stable for sizes above 35 nm (*Zhang and Banfield*).
- anatase→rutile transformation from 973 K to 1073 K; particle size increased with temperature (*Li*).

2.3 Electron Diffraction Properties

Diffraction (electron, X-Ray, neutron) represents basis in the determination of the crystal structure. All crystals have unique diffraction pattern. From comparing diffraction peaks it is possible to determine whether we are dealing with smaller or bigger particles i.e. as the nanoparticle size increase, the diffraction peaks narrow[18].

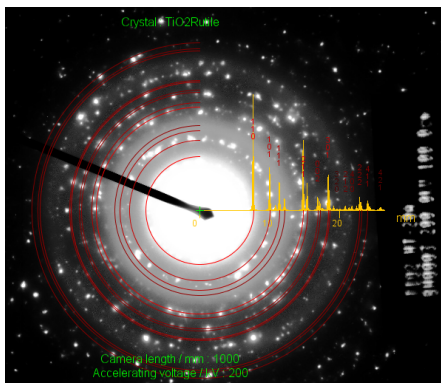


Figure 5: Electron diffraction pattern of TiO_2 sample. Theoretical model of diffraction intensities for rutile.

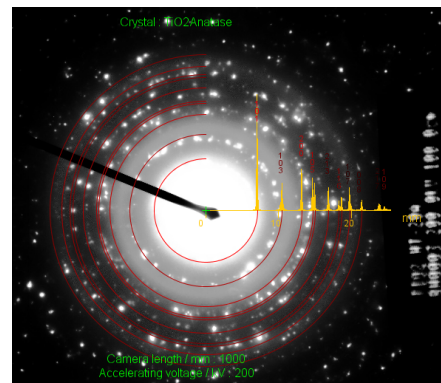


Figure 6: Electron diffraction pattern of TiO_2 sample. Theoretical model of diffraction intensities for anatase.

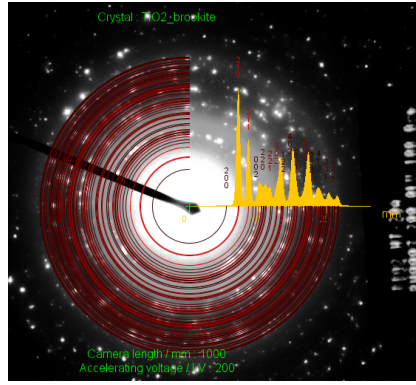


Figure 7: Electron diffraction pattern of TiO_2 sample. Theoretical model of diffraction intensities for brookite.

2.4 Raman Vibration Properties

When light is scattered on an atom, most photons are elastically scattered. This is called Rayleigh scattering. On the other hand, Raman scattering is the inelastic scattering of a photon. It can occur with a change in vibrational, rotational... energy of a molecule (when dealing with phonons). Scattered photons have different frequencies from the incident photons.

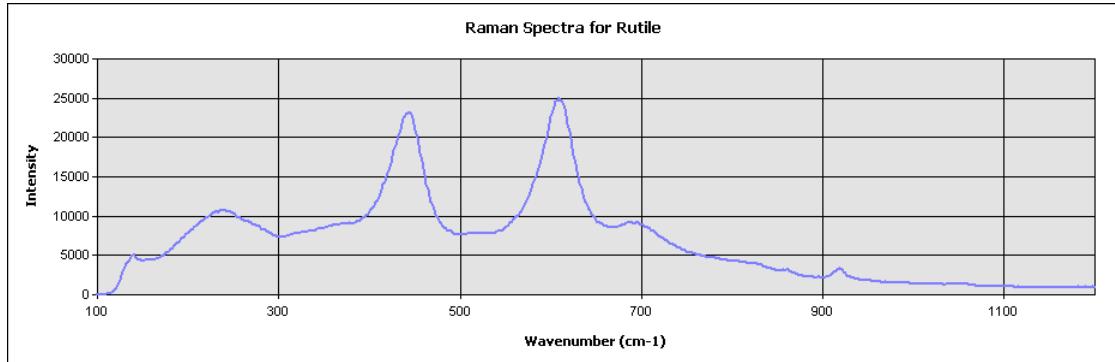


Figure 8: Raman spectra for rutile[19].

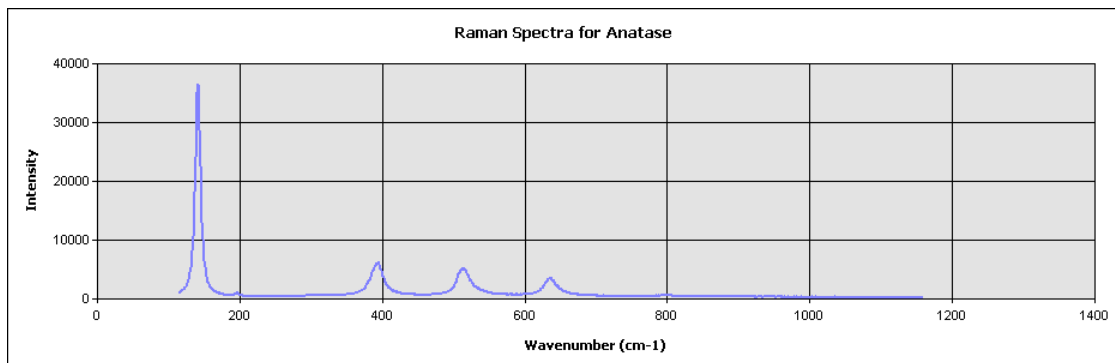


Figure 9: Raman spectra for anatase[19].

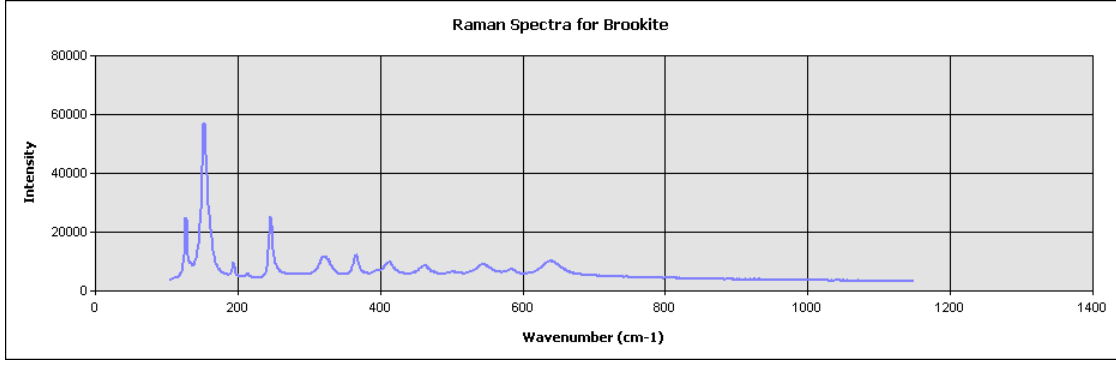


Figure 10: Raman spectra for brookite[19].

With decrease of nanoparticle size Raman scattering peaks broader[18].

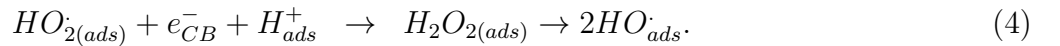
2.5 Photon-Induced Electron and Hole Properties

TiO_2 is a n-type semiconductor which is widely used as a photocatalyst. Energy gap of rutile is 3.0 eV, of anatase 3.2 eV. This is the lowest energy of impact photons needed to excite electrons from valance to unoccupied conducting band leaving behind positive holes. These photons come from UV spectra (387.5 nm for anatase[20]).

Negative electron in conductive band and positive hole in valance band represent charge carriers. They can recombine nonradiatively, radiatively (heat) or get trapped and react with electron donors or acceptors absorbed on the surface of the photocatalyst. If charge separation is maintained, the electrons and holes can migrate to the catalyst surface where they participate in redox reactions with adsorbed species. In particular, hole h_{VB}^+ may combine with H_2O or OH^- to produce the hydroxyl radical



e_{CB}^- can be picked up by oxygen to generate superoxide radicals which can in turn generate hydroperoxide and hydrogen peroxide, decomposed at the semiconductor surface into hydroxyl radicals



These very reactive radicals can oxidize the adsorbed organic pollutants to achieve complete decomposition [21].

Photocatalytic activity γ is defined as

$$\gamma = \frac{C}{3tmI}, \quad (5)$$

C is the concentration of the pollutant in units mol/l , t is the irradiation time of UV light, m is the concentration of TiO_2 particles in units g/l , I is the intensity of adsorbed UV light[22].

The photocatalytic properties of TiO_2 are affected by several factors: crystal structure, morphology and surface area. The highest photoactivity between all 3 crystal structures shows anatase. Proper mixture of anatase and rutile TiO_2 gives higher photocatalytic activity than pure anatase TiO_2 [23].

If TiO_2 is doped with metal oxide it becomes photocatalytical under visible light[18, 25, 26, 27, 28, 29, 30]. There are even some new materials (TiOBCN) related to TiO_2 which have even bigger photoreactive spectral span of light[31].

The efficiency of photocatalysis depends also on the pH of the reaction solution. The surfaces charge properties of TiO_2 change with pH. In acid conditions surface of TiO_2 is positively charged, in alkine negatively[32].

TiO_2 does not show only photocatalytical capability but also photocorrosion stability which is needed to perform reactions[23].

3 Photocatalysis Aparatus

Idea how to determine the rate of photocatalytical effect (ability to accelerate the photocatalysis of a catalyst) is to measure the decrease of concentration of a pollutant in water due to the catalyst (TiO_2 in anatase modification) which reacts with the pollutant under UV light and helps to clean the water.

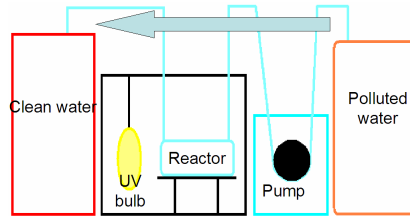


Figure 11: Scheme of apparatus used to clean water via photocatalysis.

Our test samples were from Ti6Al4V plates grown TiO_2 which were all in anatase modification. They were prepared via hydrothermal synthesis in distilled water with addition of base, TiO_2 powder and Ti6Al4V plates.

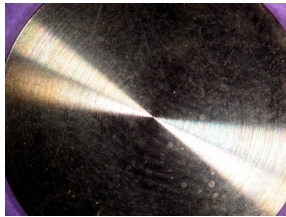


Figure 12: Picture of sample HT-34 from optical microscope.

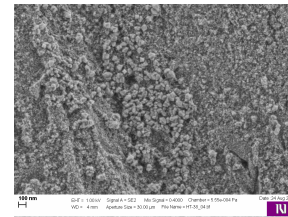


Figure 13: FEG-SEM picture of sample HT-38.

There are 2 different equipments for measuring photocatalytic activity. It depends whether material being investigated is powder (liquid) or not. When dealing with powders (liquids) cooling water jacket containing polluted water and UV bulb is used (picture 14). Otherwise, the reactor containing catalyst (Ti6Al4V plates) is just radiated with UV light which was in our case in the same closed box (UV light can damage eyes) as the reactor. However, bulb represents a closed system due to formation of O_3 in air and was constantly cooled down with water due to heating to avoid thermal reactions.

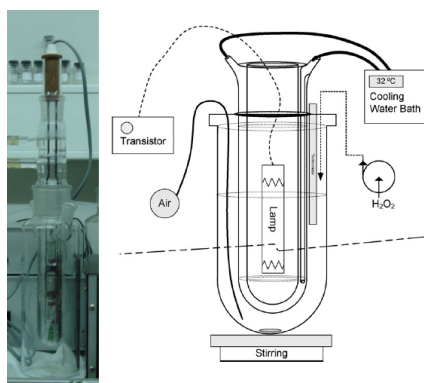


Figure 14: Picture and sheme [24] of experimental setup when dealing with powder catalysts.

There are several possibilities for nonpowder apparatus to perform photocatalysis:

1. very strong constantly cooled down UV light is in box (for eye-safety) with small aperture, reactor is far away from light source to avoid thermal reactions, for focusing the light on reactor lens is used. The weaknesses in this setup are losses of light intensity with distance.

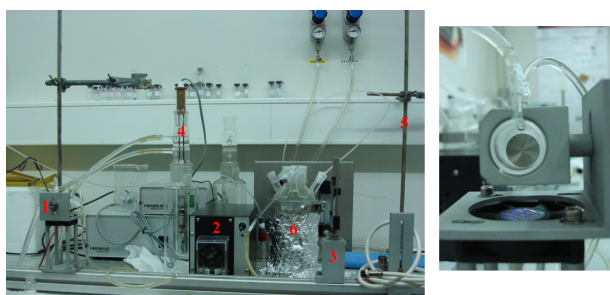


Figure 15: Photocatalysis equipment. 1 is holder of the reactor with magnetic stirrer, 2 is peristaltic pump for polluted water, 3 is lens, 4 is UV light which is when measuring on position 5 in box with small aperture, 6 is container of polluted water with constant influx of gases (Ar and O_2). Picture on right represents reactor on reactor holder containing polluted water and Ti4Al6V plates with thin layer of catalyst anatase TiO_2 .

2. very strong constantly cooled down UV light is in box (for eye-safety) along with reactor. This setup has 2 weaknesses: losses of light intensity with distance, thermal reactions.

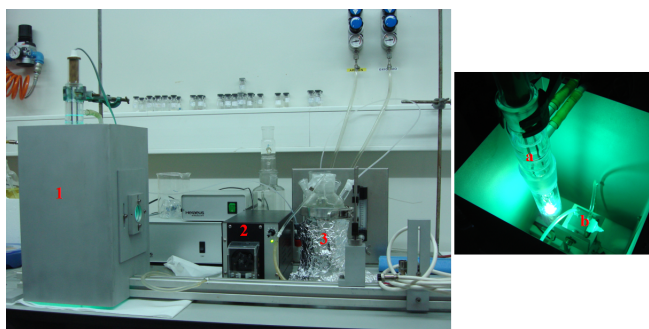


Figure 16: Experimental setup. 1 represents box containing constantly cooled down UV-bulb and reactor holder with reactor with magnetic stirrer, 2 is peristaltic pump for polluted water, 3 is container of polluted water with constant influx of gases (Ar and O₂). Picture on right shows setup of (a) UV light and (b) reactor in box.

3. very strong constantly cooled down UV light is in box with small aperture from which optical fibres transfer light to the reactor which is far away. In this way losses of intensity of UV light with distance are minimized and thermally reactions are avoided. Material surrounding UV bulb absorbs light with wavelength 185 nm which is responsible for forming ozone.¹

All glass is made from quartz because quartz is transparent for UV light. UV light has to have big spectral span to be able to activate different catalysts.

4 Measurements and results

Phenol was used as a pollutant (model solution consisted from 50 mg of phenol per liter of distilled water). Through reactor was flowing polluted water with constant current until UV light was turned on for few minutes, after that liquid was taken from reactor at given times and reactor was cleaned. Phenol transformed with photocatalysis under UV light into environment more acceptable products.

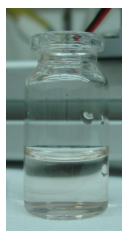


Figure 17: Polluted water changed colour after photocatalysis[33]. This is due to decomposition of phenol.

Analysis was done with computer-controlled high performance liquid chromatography (HPLC) system that measures the concentration of pollutants in polluted water [24].

¹My goal is to make described setup.

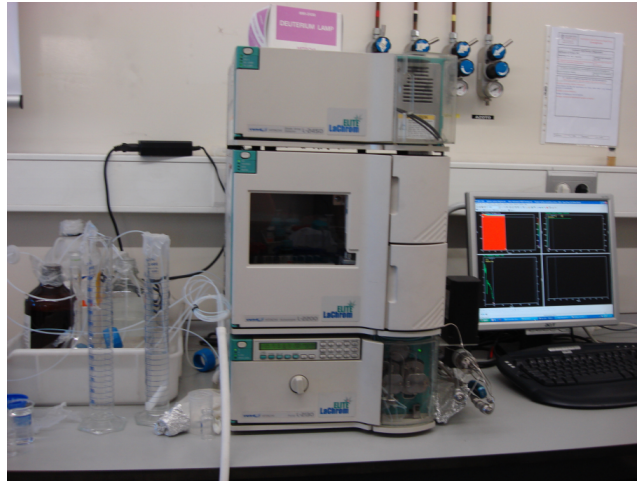


Figure 18: Equipment for high performance liquid chromatography.

Concentration of pollutant decreases with time of UV radiation. All results were normalized to measurement without catalyst to avoid mistakes arisen from thermal reactions and reactions that would happen using just UV light.

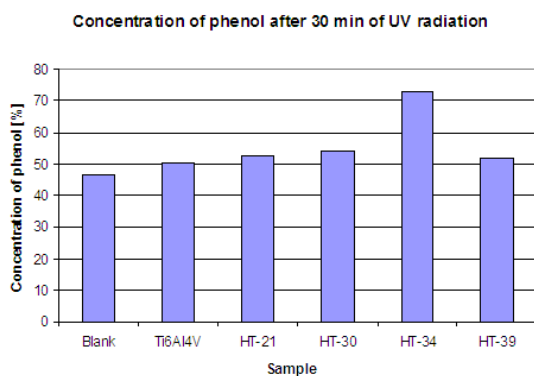


Figure 19: Concentration of phenol of 6 samples radiated for 30 min. Blank measurement represents photocatalysis dependent just on UV radiation (normalization), Ti6Al4V measurement of photocatalytical effect on plate without anatase TiO_2 layer, all other measurements are on samples with TiO_2 layers.

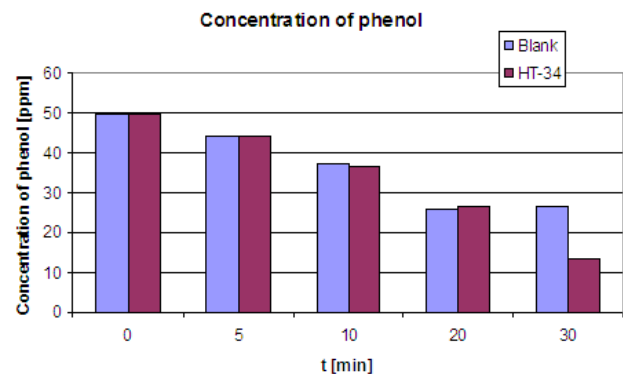


Figure 20: Concentration of phenol after UV radiation for different time on sample HT-34 and on polluted water without catalyst (blank measurement).

From all samples only one showed photocatalytical properties after 30 minutes of UV radiation. This sample (HT-34) has the smallest particles on the surface that reflects in much bigger number of reactive places for photocatalysis.

5 Conclusion

Nowadays, when population is environmentally aware, is capability of photocatalysis of TiO_2 one of the most appreciated properties of TiO_2 . Due to this property there are several applications con-

cerning cleaning of surfaces and cleaning of waste-water. But most important application in research on K7 on Jožef Stefan Institute is capability of photocatalysis of TiO_2 anatase thin film on Ti6Al4V surfactants for usage in medicine i.e. for artificial implants.

Anatase TiO_2 grew on Ti6Al4V plates during hydrothermal synthesis. These plates were UV radiated i.e. reactive places for photocatalysis were activated. Photocatalytical effect was measured via lowering the concentration of added impurities into water. Results were normalized onto measurement without any catalyst to avoid mistakes because of direct reaction of UV light with impurities and because of thermal reactions. Between all 6 tested samples only sample HT-34 showed photocatalytical activity after 30 min of radiation.

References

- [1] j. Yoon, E. Shim, S. Bae, H. Joo. *Application of immobilized nanotubular TiO_2 electrode for photocatalytic hydrogen evolution: Reduction of hexavalent chromium (Cr(VI)) in water*. Journal of Hazardous Materials, 161, 1069-1074, 2009.
- [2] A. H. Fostier, M. do Socorro Silva Pereira, S. Rath, J. R. Guimaraes. *Arsenic removal from water employing heterogeneous photocatalysis with TiO_2 immobilized in PET bottles*. Science Direct, Chemosphere 72, 319-324, 2008.
- [3] E. Sanchez Mora, E. Gomez Barojas, E. Rojas Rojas, R. Silva Gonzalez. *Morphological, optical and photocatalytic properties of $\text{TiO}_2\text{-Fe}_2\text{O}_3$ multilayers*. Science Direct, 91, 1412-1415, 2007.
- [4] C. Gomes Silva, W. Wang, J. L. Faria. *Photocatalytic and photochemical degradation of mono-, di- and tri-azo dyes in aqueous solution under UV irradiation*. Science Direct, 181, 314-324, 2006.
- [5] A. Franco, M. C. Nves, M. M. L. Ribeiro Carrott, M. H. Mendonca, M. I. Pereira, O. C. Monteiro. *Photocatalytic decolorization of methylene blue in the presence of TiO_2/ZnS nanocomposites*. Journal of Hazardous Materials, 161, 545-550, 2009.
- [6] M. Mahalakshmi, S. Vishnu Priya, B. Arabindoo, M. Palanichamy, V. Murugesan. *Photocatalytic degradation of aqueous propoxur solution using TiO_2 and $H\beta$ zeolite-supported TiO_2* . Journal of Hazardous Materials, 161, 336-343, 2009.
- [7] W. Wang, C. Gomes Silva, J. L. Faria. *Photocatalytic degradation of Chromotrope 2R using nanocrystalline TiO_2 /activated-carbon composite catalysts*. Science Direct, 70, 470-478, 2006.
- [8] J. Sa, C. Alcaraz Aguera, S. Gross, J. A. Anderson. *Photocatalytic nitrate reduction over metal modified TiO_2* . Science Direct, 85, 192-200, 2009.
- [9] B. Tryba, M. Piszcz, B. Grzmil, A. Pattek-Janczyk, A. W. Moravski. *Photodecomposition of dyes on $\text{Fe} - \text{C} - \text{TiO}_2$ photocatalysts under UV radiation supported by photo-Fenton process*. Journal of Hazardous Materials, 162, 111-119, 2009.
- [10] C. A. Silva, L. M. Madeira, R. A. Boaventura, C. A. Costa. *Photo-oxidation of cork manufacturing wastewater*. Chemosphere, 55, 19-26, 2004.
- [11] J. C. Garcia, J. I. Simionato, A. E. Carli da Silva, J. Nozaki, N. Evelazio de Souza. *Solar photocatalytic degradation of real textile effluents by associated titanium dioxide and hydrogen peroxide*. Science Direct, article in press.
- [12] S. Wang, Q. Gongm, J. Liang. *Sonophotocatalytic degradation of methhy orange by carbon nanotube TiO_2 in aqueous solutions*. Ultrasonic Sonochemistry, 16, 205-208, 2009. 13
- [13] A. M. T. Silva, E. Nouli, A. C. Carmo-Apolinario, N. P. Xekoukoulotakis, D. Mantzavinos. *Sonophotocatalytic H_2O_2 degradation of phenolic compounds in agro-industrial effluents*. Science Direct, 124, 232-239, 2007.
- [14] M. Inagaki, N. Kondo, R. Nonaka, E. Ito, M. Toyoda, K. Sogabe, T. Tsumura. *Structure and photoactivity of titania derived from nanotubes and nanofibers*. Journal of Hazardous Materials, 161, 1514-1521, 2009.

- [15] G. Tian, H. Fu, L. Jing, C. Tian. *Synthesis and photocatalytic activity of stable nanocrystalline TiO₂ with high crystallinity and large surface area*. Journal of Hazardous Materials, 161, 1122-1130, 2009.
- [16] Wikipedia, The Free Encyclopedia. <http://en.wikipedia.org/wiki/TiO2>. Last accessed on 27. 1. 2009.
- [17] Crystal Lattice-Structures. <http://cst-www.nrl.navy.mil/lattice/>. Last accessed on 27. 1. 2009.
- [18] X. Chen, S. Mao. *Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications*. Chemical Reviews, 107, 2891-2959, 2007.
- [19] Raman Spectroscopy, Uniersita di Siena. <http://www.dst.unisi.it/geofluids/raman/spectrum.frame.htm>. Last accessed on 27. 1. 2009.
- [20] C.-J. Chung, H.-I. Lin, C.-M. Chou, P.-Y. Hsieh, C.-H. Hsiao, Z.-Y. Shi, J.-L. He. *Inactivation of Staphylococcus aureus and Escherichia coli under various light sources on photocatalytic titanium dioxide thin film*. Surface & Coatings Technology, 203, 1081-1085, 2009.
- [21] M. Fassier, N. Chouard, C. S. Peyratout, D. S. Smith, H. Riegler, D. G. Kurth, C. Ducroquertz, M. A. Bruneaux. *Photocatalytic activity of oxide coatings on fired clay substrates*. Science Direct, 29, 565-570, 2009.
- [22] C. H. Cho, D. K. Kim. *Photocatalytic Activity of Monodispersed Spherical TiO₂ Particles with Diferent Crystallization Routes*. Journal of the American Ceramic Society, 86 [7], 1138-45, 2003.
- [23] G. Xu, Z. Zheng, Y. Wu, N. Feng. *Effect of silica on the microstructure and photocatalytic properties of titania*. Science Direct, 35, 1-5, 2007.
- [24] A. M. T. Silva, E. Nouli, N. P. Xekoukoulotakis, D. Mantazavinos. *Effect of key operating parameters on phenols degradation during H₂O₂-assisted TiO₂ photocatalytic treatment of simulated and actual olive mill wastewaters*. Science Direct, 73, 11-22, 2007.
- [25] K. Lv, H. Zuo, J. Sun, K. Deng, S. Liu, X. Li, D. Wang. *(Bi, CandN) codoped TiO₂ nanoparticles*. Journal of Hazardous Materials, 161, 396-401, 2009.
- [26] J. Li, J. Xu, W.-L. Dai, H. Li, K. Fan. *Direct hydro-alcohol thermal synthesis of special core-shell structured Fe-doped titania microspheres with extended visible light response and enhanced photoactivity*. Science Direct, 85, 162-170, 2009.
- [27] Y. Yang, H. Wang, X. Li, C. Wang. *Electrospun mesoporous W⁶⁺-doped TiO₂ films for efficient visible-light photocatalysis*. Materials Letters, 63, 331-333, 2009.
- [28] J. Geng, D. Yang, J. Zhu, D. Chen, Z. Jiang. *Nitrogen-doped TiO₂ nanotubes with enhanced photocatalytic activity synthesized by a facile wet chemistry method*. Materials Research Bulletin, 44, 146-150, 2009.
- [29] R. Jin, Z. Wu, Y. Liu, B. Jiang, H. Wang. *Photocatalytic reduction of NO with NH₃ using Si-doped TiO₂ prepared by hydrothermal method*. Journal of Hazardous Materials, 161, 42-48, 2009.
- [30] J.W. Shi, J.-T. Zheng, P. Wu. *Preparation, characterization and photocatalytic activities of holmium-doped titanium dioxide nanoparticles*. Journal of Hazardous Materials, 161, 416-422, 2009.

- [31] L. Zhang, X. Li, Z. Mou, S. Wang, F. He. *Amorphous TiOBCN - A new solar photocatalyst*. Materials Letters, 63, 165-167, 2009.
- [32] A. R. Khataee, V. Vatanpour, A. R. Amani Ghadim. *Decolorization of C. I. Acid Blue 9 solution by UV/Nano-TiO₂, Fenton, Fenton-like, electro-Fenton and electroagulation processes: A comparative study*. Journal of Hazardous Materials, 161, 1225-1233, 2009.
- [33] S. Nahar, K. Hasegawa, S. Kagaya, S. Kuroda. *Adsorption and aggregation of Fe(III)–hydroxy complexes during the photodegradation of phenol using the iron-added-TiO₂ combined system*. Journal of Hazardous Materials, 162, 351-355, 2009.