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Modyfication of photocatalytic properties of titanium dioxide by mechano-chemical method

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The paper presents a simple way to improve the photocatalytic properties of titanium dioxide using mechano-chemical method. The TiO_2 (Anatase) powders was subjected to high-energy ball milling in dry environment and in methanol. It has been shown that it is possible to induce the phase transformation from Anatase to Rutile and produce a material with a higher photocatalytic activity in the UV light. Physicochemical characteristics of the products were based on the following methods and techniques: X-ray powder diffraction (XRD), IR and UV-Vis (DR) spectroscopy, measurements of specific surface area (BET). The photocatalytic activity of the powders was measured in the decomposition reaction of methyl orange in water.

Keywords: mechanochemistry, high-energy ball milling, titanium dioxide, photocatalysis.

INTRODUCTION

Technological advancements associated with the development of industry caused considerable environmental pollution. Especially in large industrial centers and conurbations the limit values for concentrations of harmful substances in surface waters are becoming increasingly exceeding. Removal of organic pollutants from water in a large scale is particularly difficult and especially very costly. Therefore are constantly looking for new methods of water purification.

One of the proposed solutions are Advanced Oxidation Processes (AOP), whose main characteristic is the preparation of highly oxidizing hydroxyl radical[1, 2]. An example of such process is the photocatalysis which, in contrast to the conventional methods of water purification (eg. coagulation or adsorption on activated carbon) does not transfer contaminants form one phase to another but leads to a complete decomposition of the organic compounds. Such reactions occur in an aqueous medium in the presence of a photocatalyst which is activated by light with appropriate energy. Most currently used photocatalysts are transition metal compounds from which, due to small band gap, low toxicity and the price the most popular is titanium dioxide[5]. The value of the energy band gap of TiO_2 is about 3.2eV means that for activation of this semiconductor is required light witch a wavelength above 360 nm, which corresponds to UV radiation. Due to the small proportion of UV radiation in sunlight (about 5%), it is necessary to use artificial sources of this light which further increases the cost of the process.

The ongoing scientific research are focused on the modification of titanium dioxide to allow its activation by wisible light[5–8]. This effect can be achieved by an appropriate modification of the crystal structure of the semiconductor (eg. doping by various elements). The presence of modifier also prevents the recombination process. This involves a higher photocatalytic activity under visible light.

The most popular methods for modifications of titanium dioxide are sol-gel and hydrothermal techniques. However, due to high production costs, complicated equipment and high arduousness for the environment chemists are constantly looking for new, effective and low-cost methods for production of active under visible light photocatalysts.

The purpose of this study was to determine the possibility of modifying the crystal structure of TiO_2 in order to increase its photocatalytic activity in the visible light using high energy ball milling technique[9].

EXPERIMENTAL

Preparation procedure

In this study, the modification of titanium dioxide was performed using a simple mechanochemical method[9]. The raw powders (TiO_2 – anatase, 25 nm, Sigma-Aldrich, 99,7% pure) were subjected to high-energy ball milling process for a 0-3 hours. The milling was carried out in two series: I – dry milling and II – wet milling in the presence of methanol (Methanol anhydrous, Avantor, 99,8% pure). The mass ratio of alcohol to the TiO_2 was 1:1. Mechanochemical processing of powders was carried out using planetary high-energy ball mill *Pulverisette-6* Fritsch GmbH. The vessel (250 ml) and balls of 10 mm in diameter of zirconia were used. The grinding was operates of 500 rpm for various period of time ranged from 0.5 to 3 hours with ball to powder mass ratio (BPR) of 20:1. The ground powders were subsequently heated in air at 200°C and 400°C for 60 min in Nabertherm HTC 03/15 laboratory furnace.

Measurements' techniques

The as-synthesized materials were analyzed via a powder X-ray diffraction with a CuKα source on an X'Pert Philips instrument, for $2\theta = 10^o - 90^o$ with a step size of 0.01^0. The identification of the material was made according to a JCPDS table. The crystallite size was calculated by Scherrer's formula[10] and the average crystallite size (D) was calculated by following equation:

$$D = D_A\left(\frac{I_A}{I_A+I_R}\right) + D_R\left(\frac{I_R}{I_A+I_R}\right)$$

were D_A and D_R are crystallite size of anatase and rutile. I_A and I_B are peak intensity of anatazse (101) and rutile (110) respectively.

The surface area of the materials was determined using BET (Brunauer, Emmet and Teller) physical adsorption isotherms. Measurements were taken using an Accelerated Surface Area and Porosimetry Analyzer (ASAP) 2020 from Micrometrics. The optical absorption edge of the products was measured by an UV-Vis DR (Specord 205) Analytik JenaAG. The chemical composition of the surface of obtained powders were studied on the basis of the absorption spectra in the range (4000–400 cm^{-1}) with a spectra resolution of 4 cm^{-1} using a Digilab Scimitar Series FTS2000 spectrophotometer. The photocatalytic activity of the materials was tested in the decomposition reaction of methyl orange in water. Experiments were carried out in a dark and closed box witch UV radiation source, 12W low-pressure mercury lamp (Krüss Optronic) with a wavelength of 254 nm, 366 nm and artificial visible light <510 nm. The light wavelength was controlled by selecting various filter. A 2ppm metyl orange solution with photocalyst (0.2 g/dm^3) were magnetically stirred in 25 cm^3 beaker. Before turning on the light source, photocatalysts were stirred in a dark for 60 min to achieve adsorption equilibrium. The samples were taken regularly at 30 minute intervals. The concentration of the dye was measured by UV-Vis Specord 205 Analytik Jena spectrophotometer.

RESULTS AND DISCUSSION

Effects of mechanochemical treatment on structure of titanium dioxide

The X-ray diffraction patterns of the titanium dioxide subjected to mechanochemical treatment in air at various period of time was shown in Figure 1. The effect of high-energy ball milling on phase transition of TiO_2 is clearly visible. 30 minutes of mechanochemical treatment led to the transformation of the structure from anatase form to rutile. This sample showed the existence of two phases – rutile and anatase.

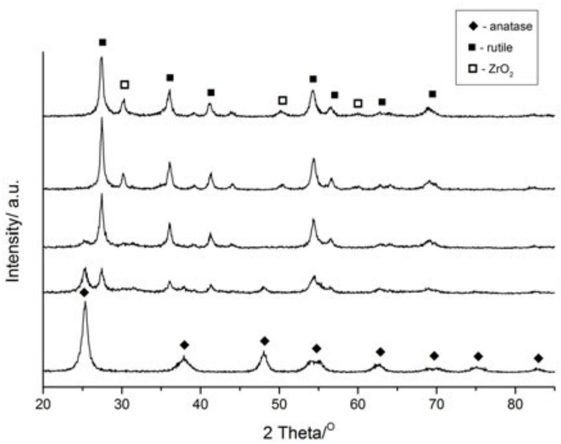

Figure 1. X-ray diffraction patterns of TiO_2 subjected to mechanochemical treatment in air

Further high energy treatment leads to the disappearance of anatase phase and formation of a dominant rutile phase. Sample subjected to 2 hours of mechanochemical treatment was characterized by only rutile phase. In addition to phase transition, high-energy ball milling has also led to significant grain reduction of the material. Both of these factors are crucial to achieve high photocatalytic activity of TiO_2.

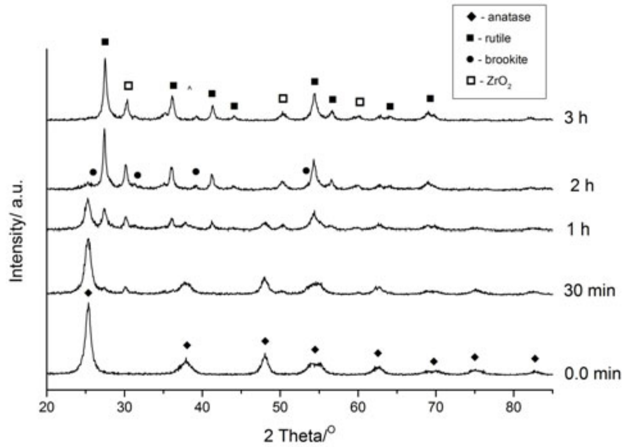

Figure 2. X-ray diffraction patterns of TiO_2 subjected to mechanochemical treatment in the presence of methanol

Figure 2 X-ray diffraction patterns of TiO_2 subjected to mechanochemical treatment in the presence of methanol

The results of analogous series of milling but in the presence of methanol are shown in Figure 2. As well as in the previous case, high-energy ball milling has led to phase transition of titanium dioxide, but in this case, applied a wet environment of mechanochemical process, affects on stabilization of anatase phase. In order to achieve this transformation was necessary to use twice as long milling, i.e. 1 hour. This structural phase transition as in the previous case occurred successively during the process, changing the percentage share of anatase to rutile phase. To obtain monophasic rutile phase, 3 hours of high-energy ball milling was necessarily. It turns out that using milling in methanol can be obtained very rare polymorphic form of TiO_2 which is brookite. This phase appeared after 2 hours of grinding. Mechanochemical treatment also in this case led to a reduction of grain sizes of powder. In this way obtained a smaller particle size than the dry milling (Fig. 3). In both cases it was also observed the presence of ZrO_2 phase derived from grinding media in the milling process. This phenomenon is well known and widely discussed in the works[11, 12].

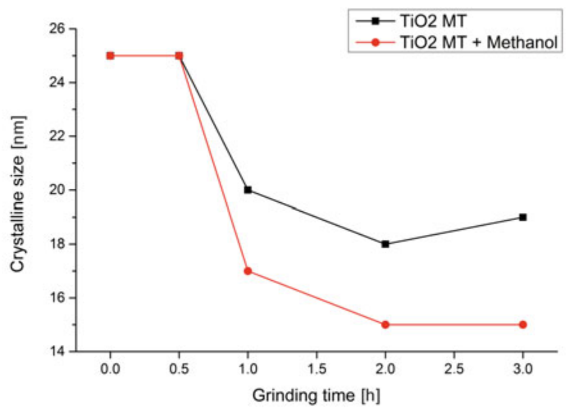

Figure 3. Average grain size of TiO_2 after mechanochemical treatment in air and methanol

Apart from size reduction and changing the phase composition i also clearly visible the influence of mechanochemical processing in methanol on the chemical composition of the surface of the photocatalyst. This is confirmed by the IR spectra of TiO_2 powders shown in Figure 4. Characteristic vibrations corresponding to different alcohol-related products located in the range 1050–1450 cm^{-1}, water and hydroxyl groups (1620–1630 cm^{-1}) indicate the progressive decomposition of methanol on TiO_2[13, 14]. The powder also changed color from white to black. The vibrations corresponding to the decomposition products of methanol disappear after calcining the powder at 400°C.

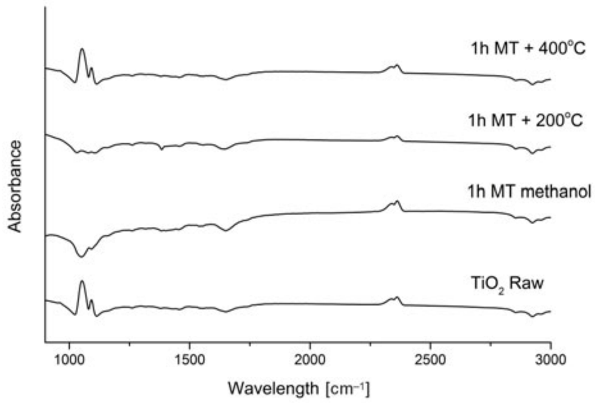

Figure 4. IR spectra of raw TiO_2; powder milling for 1h in methanol and subsequent calcination at 200 and 400°C

Mentioned modification of TiO_2 also changes its spectroscopic properties. Effect of the presence of methanol during milling on increase the absorption of electromagnetic radiation in the visible light range of the product is evident. Milling the powder without the addition of methanol does not significantly increase the absorbance of TiO_2 in the visible light (Fig. 5).

High-energy ball milling also results significant reduction of the powder grain size, which causes increase its specific BET surface area (Fig. 6). The subsequent calcination of the modified TiO_2 causes a slight increase in crystallite size and a decrease in BET specific surface area.

Study of photocatalytic activity of powders

The photocatalytic activity tests was performed for samples milling in the presence of methanol and subsequent calcination at 200 and 400°C. As a reference

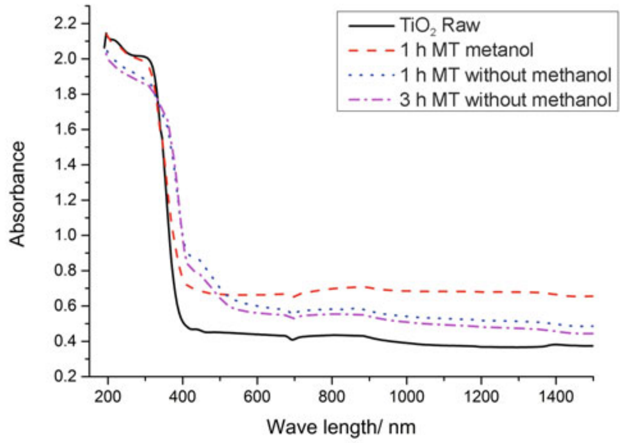

Figure 5. UV-Vis diffuse reflectance spectra of pure and subjected to mechanochemical treatment TiO_2

material was used the starting TiO_2 powder. The effect of modifications on the photocatalytic activity of materials is clearly visible (Fig. 7).

All TiO_2 samples ground in the presence of methanol exhibited higher, compared to the reference sample, photocatalytic activity in the decomposition of the dye in tested wavelength ranges. Exceptions were the powders subjected to calcination at 200 and 400°C, which under ultraviolet light (256 nm) showed a lower photoactivity. These observations are similar to results reported by other authors[15, 16]. Thermal treatment caused an increase crystallite size, lower BET specific surface area and

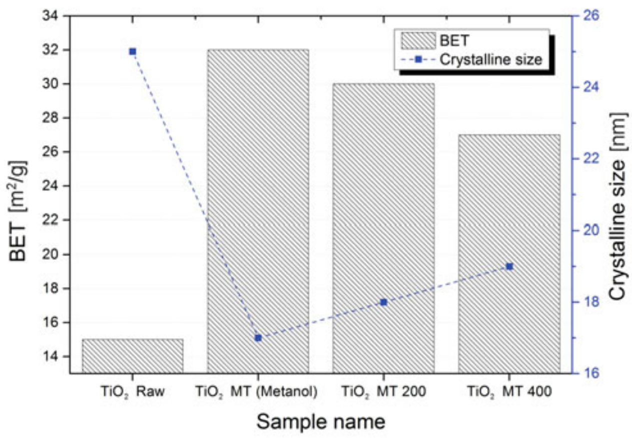

Figure 6. BET specific surface area and average crystallite size of the starting and modified TiO_2

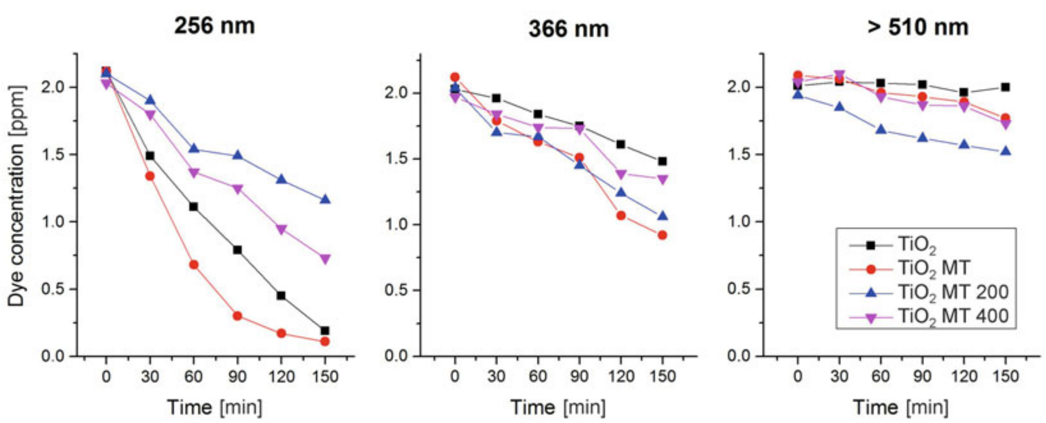

Figure 7. Concentration of dye on the exposure time for suspension with photocatalyst by light with different wavelength for raw and modified TiO_2

a larger amount of rutile phase in the sample, which results in a reduced photocatalytic activity in the UV. Each of the modified samples had also higher, relative to a reference sample photocatalytic activity in the light with wavelength of 366 nm. Such a high photocatalytic activity was caused by the presence of carbon ions deriving from the decomposition of methanol, which in the calcination process was partially substituted into TiO_2 crystal structure reducing the band gap. In addition, the doping of TiO_2 with carbon, promotes the formation of oxygen vacancies, which also affects on the higher photocatalytic activity of such materials. In the visible light we observed a slight docolorization of dye solution on modified TiO_2. This effect is probably by the effect of sensitization of titanium dioxide.

SUMMARY

Presented in the paper method of modifying titanium dioxide allow to obtain a material with high photocatalytic activity in UV light with the wavelength 256 and 366 nm. The effect of sensitization of TiO_2 leads to decolorization of the dye soliution in visible light. Increase in photocatalytic activity under UV light, of TiO_2 subjected to mechanochemical treatment in methanol is mainly due to the presence of carbon, derived from the decomposition of methanol.

Mechanochemical treatment regardless of the used milling conditions (with or without methanol) leads to induce phase transition of TiO_2 (Anatase to Rutile), reduction of particle size, BET specific surface area and the absorption of electromagnetic radiation in the visible light. In the consequence of high energy ball milling in the presence of methanol the modification of surface of TiO_2 take place, which affects the slowing down the process of transformation of Anatase to Rutile. Moreover a high-energy ball milling in methanol allows to obtain a rare polymorphic form of titanium dioxide – Brookite.

ACKNOWLEDGEMENT

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LITERATURE CITED

1. Prado, J. & Esplugas, S. (1999) Comparison of different advanced oxidation processes involving ozone to eliminate atrazine. *Ozone Sci. Eng.* 21(1), 39–52. DOI: 10.1080/01919519908547258.
2. Homem, V. & Santos, L. (2011) Degradation and removal methods of antibiotics form aqueous matrices – A review. *J. Environ. Manage*. 92(10), 2304–2347. DOI: 10.1016/j.jenvman.2011.05.023.
3. Manyala, R. Ed. (2010). *Solar Collectors and Panels, Theory and Applications.* Rikea: INTECH.
4. Mills, A. & Hunte, S.L. (1997). An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A: Chem*. 108, 1–35. DOI: 10.1016/S1010-6030(97)00118-4.
5. Chen, X. & Mao, S.S. (2007). Titanium Dioxide nanomaterials: Synthesis, Properties, Modifications and Applications. *Chem. Rev.* 107, 2891–2959. DOI: 10.1021/cr0500535.
6. Carp, O., Huisman, C.L. & Reller, A. (2004) Photoinduced reactivity of titanium dioxide. *Progr. Sol. State Chem*. 32, 33–177. DOI: 10.1016/j.progsolidstchem.2004.08.001.
7. Marschall, R. & Wang, L. (2014). Non-metal doping of transition metal oxides for visible-light photocatalysis. *Cat. Today* 225, 111–135. DOI: 10.1016/j.cattod.2013.10.088.
8. Zong, X. & Wang, L. (2014). Ion-exchangeable semiconductor materials for visible light-induced photocatalysis, *J. Photochem. Photobiol. C: Photochem. Rev.* 18, 32–49. DOI: 10.1016/j.jphotochemrev.2013.10.001.
9. Balaz, P. (2008). *Mechanochemistry in Nanoscience and Minerals Engineering*, Berlin, Heidelberg, Springer.
10. Dinnebier, R.E. & Brillinge, S.J.L. Eds. (2008). *Powder Diffraction Theory and Practice,* Cambridge, RSC Publishing.
11. Dulian, P. (2016). Solid-State Mechanochemical Syntheses of Perovskites. In Pan, L. & Zhu, G. *Perovskite Materials – Synthesis, Characterisation, Properites, and Applications* (3–26) Rikea, INTECH.
12. Senna, M. (2007). Smart mechanochemistry-Charge transfer control for tailored solid-state under minimum external energy. *J. Alloy. Compd.* 434, 768–772. DOI: 10.1016/j.jallcom.2006.08.238.
13. Gamal, A., Hussein, M., Sheppard, N., Mohamed, I.Z. & Radamis, B.F. (1991). Infrared Spectroscopic Studies of the Reactions of Alcohols over Group IVB Metal Oxide Catalysts Part 2. Methanol over TiO_2, ZrO_2 and HfO_2 *J. Chem. Soc. Faraday Trans*. 87(16), 2655–2659. DOI: 10.1039/FT9918702655.
14. Gamal, A., Hussein M., Sheppard N., Mohamed, I.Z. & Radamis, B.F. (1991). Infrared Spectroscopic Studies of the Reactions of Alcohols over Group IVB Metal Oxide Catalysts Part 3. – Ethanol over TiO_2, ZrO_2 and HfO_2 and General Conclusions from Parts 1 to 3. *J. Chem. Soc. Faraday Trans.* 87(16), 2661–2668. DOI: 10.1039/FT9918702661.
15. Reddy, K.M., Reddy, C.V.G. & Manorama, S.V. (2001) Preparation, characterization and spectral studies on nanocrystalline anatase TiO_2 *J. Solid State Chem.* 158, 180–186. DOI: 10.1006/jssc.2001.9090.
16. Fujishima, A., Zhang, X. & Tryk, D.A. (2008). TiO_2 photocatalysis and related surface phenomena. *Surf. Sci. Rep.* 63(12), 515–582. DOI: 10.1016/j.surfrep.2008.10.001.