

# Preparation of TiO<sub>2</sub>-Nitrogen-Doped Photocatalyst Active under Visible Light

Beata Wawrzyniak, Antoni Waldemar Morawski, and Beata Tryba

*Faculty of Chemical Engineering, Szczecin University of Technology, Pułaskiego 10, 70-322 Szczecin, Poland*

Received 16 February 2006; Revised 20 June 2006; Accepted 21 June 2006

This study examined the photocatalytic degradation of phenol and azo dyes such as Reactive Red 198 and Direct Green 99 by photocatalysis over amorphous hydrated titanium dioxide (TiO<sub>2</sub> · H<sub>2</sub>O) obtained directly from the sulphate technology installation modified in gaseous ammonia atmosphere. The photocatalysts were used in the solution and coated on the glass plate after sandblasting. The highest rate of phenol degradation in the solution was obtained for catalysts calcinated at 700°C (6.5% wt.), and the highest rate of dye decolorization was found for catalysts calcinated at 500°C and 600°C (ca. 40%–45%). Some TOC measurements of dye solutions were performed to check the rate of mineralization. On the glass plate, the decomposition of DG99 on TiO<sub>2</sub>/N 500 contrary to TiO<sub>2</sub>-P25 proceeded completely after 120 hours of visible light irradiation. The prolongation of the time of irradiation did not enhance DG99 degradation on TiO<sub>2</sub>-P25. The decomposition of the Direct Green 99 on TiO<sub>2</sub>/N 500 coated on the glass plate covered with liquid glass took place up to 24 hours of irradiation. The liquid layer on the glass plate which was covered with the photocatalyst reduced its activity. The nitrogen doping during calcinations under ammonia atmosphere is a new way of obtaining a photocatalyst which could have a practical application in water treatment system under broadened solar light spectrum as well as self-cleaning coatings.

Copyright © 2006 Beata Wawrzyniak et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

## 1. INTRODUCTION

TiO<sub>2</sub> semiconductor in anatase form is a very often used photocatalyst for water purification from pollutants because of its stability, nontoxicity, and a relatively satisfied activity. However, anatase has a high energy of the band gap ( $E_G > 3.2$  eV), and therefore could be excited by UV radiation only ( $\lambda < 380$  nm). Moving of the absorption spectrum of TiO<sub>2</sub> into the visible region  $\lambda > 400$  nm is the subject of challenge for utilization of renewable energy source.

It was described by Asahi et al. [1, 2] that TiO<sub>2-x</sub>N<sub>x</sub> films which were prepared by sputtering the TiO<sub>2</sub> target in an N<sub>2</sub> (40%)/Ar gas mixture followed by annealing at 550°C in N<sub>2</sub> gas absorbed visible light at the wave range less than 500 nm. The authors concluded that visible light absorption by N-doped TiO<sub>2</sub> was due to the substitution of oxygen by nitrogen, which resulted in mixing of N(2p) with O(2p) states. Ihara et al. [3] prepared a VIS-active photocatalyst by the calcinations of the hydrolysis products of Ti(SO<sub>4</sub>)<sub>2</sub> treated with NH<sub>3</sub> aqua solution. The colors of obtained samples were of yellow or bluish-green that absorbed light in the blue (400 nm) to bluish-green (550 nm) regions exclusively. Authors detected nitrogen in their samples and

they concluded that oxygen-deficient sites formed in the grain boundaries were important as the blockers for reoxidation.

Azo dyes are a class of colored organic compounds that have been extensively used in both industry, such as textiles, papers, cosmetics, and in analytical chemistry. About a half of global production of synthetic textile dye is classified to azo compounds that have the chromophore of –N=N– unit in their molecular structure. These azo dyes are known to be largely nonbiodegradable in aerobic conditions and known to be reduced to more hazardous intermediates in anaerobic conditions. It is well known that soluble azo dyes can cause cancer on human beings. Removing color of dyes is clearly visible and influences the quality of water considerably. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove color from textile effluents. One of the new methods of wastewater treatment containing dyes is their photocatalytic degradation in the solutions illuminated with VIS irradiation, which contain the suitable photocatalyst, mainly TiO<sub>2</sub>, due to its easy access, low price, and chemical stability. This method was successfully applied to the decomposition of numerous organic substances, including azo dyes (Stylidi et al. [4], Kuo

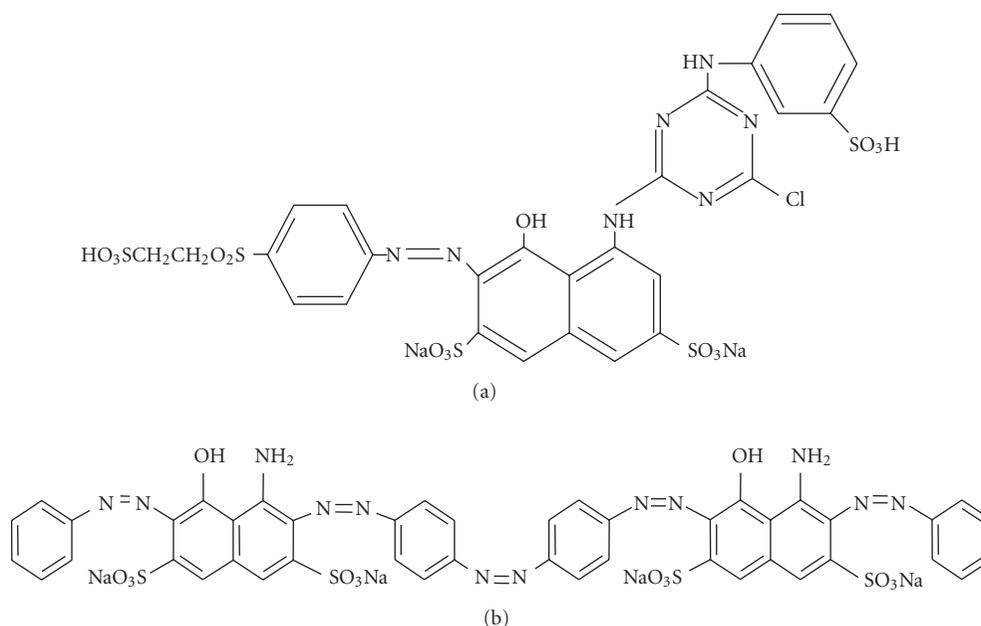


FIGURE 1: The chemical structure of (a) Reactive Red 198 and (b) Direct Green 99.

and Ho [5]). It has been found that the substitutional N-doping is a very effective method of preparation of VIS-active photocatalysts (Ihara et al. [3], Burda et al. [6], Gole et al. [7]). Over the past few years, a large amount of work has been done on the photosensitization of semiconductors such as TiO<sub>2</sub> by a variety of colored organic compounds, for example, Wang [8]. One reason for this interesting result derived from their ability is to extend the photoreponse of large-bandgap semiconductors to the visible region. Although TiO<sub>2</sub> Aeroxide P25 (Degussa, Germany) has been used in a major part to degrade a large variety of organic compounds, several researches have developed new titania materials with different structural and textural properties (Guillard et al. [9], Herrmann et al. [10]).

## 2. EXPERIMENTAL

The aim of the present work was to obtain visible light active photocatalyst by calcination of amorphous hydrated titanium dioxide (TiO<sub>2</sub> · H<sub>2</sub>O) directly from the sulphate technology installation in gaseous ammonia atmosphere. The photocatalytic activity of obtained photocatalysts was investigated under visible light through the degradation of azo dyes Reactive Red 198 ( $\lambda_{\max} = 518$  nm), Direct Green 99, ( $\lambda_{\max} = 624$  nm), and phenol ( $\lambda_{\max} = 269$  nm). In this paper, we also present the decolorization of azo dye Direct Green 99 on the glass plate after sandblasting.

### 2.1. Materials

The commercially available azo dyes such as the Reactive Red 198 (C<sub>24</sub>H<sub>20</sub>N<sub>7</sub>Na<sub>2</sub>O<sub>16</sub>S<sub>5</sub>Cl) and the Direct Green

99 (C<sub>44</sub>H<sub>28</sub>N<sub>12</sub>Na<sub>4</sub>O<sub>14</sub>S<sub>4</sub>) produced by Chemical Factory Boruta-Color Sp. z o.o. (Poland), and phenol were used as the model compounds. A chemical structure of the azo dyes is presented in Figure 1.

Titanium dioxide Aeroxide TiO<sub>2</sub>-P25 was supplied by Degussa company (Germany). The industrially produced Police SA (Poland) amorphous hydrated titanium dioxide (TiO<sub>2</sub> · H<sub>2</sub>O) containing nuclei of rutile in ratio 3.5% to TiO<sub>2</sub> w/w was obtained directly from the sulphate technology installation and used as a precursor for photocatalyst preparation. The TiO<sub>2</sub> catalyst was supplied by Chemical Factory "Police" SA (Poland).

A commercially available glass plate after sandblasting was used as a support for the catalyst.

### 2.2. Preparation of modified photocatalyst samples

The crude of amorphous hydrated titanium dioxide was washed off three times with ammonia water (NH<sub>3(aq)</sub>) and then with distilled water in order to remove sulfate ions. Such obtained catalyst was dried in an oven at 100°C for 17 hours (amorphous TiO<sub>2</sub> treated with NH<sub>3(aq)</sub>). The nitrogen-doped catalysts (TiO<sub>2</sub>/N) were obtained by heating TiO<sub>2</sub> for 4 hours in the gaseous NH<sub>3</sub> atmosphere. The calcination temperatures ranged from 200°C to 800°C, respectively. The modification of TiO<sub>2</sub> · H<sub>2</sub>O was conducted in the pipe furnace (type R40/250/12-C40 Nabertherm, Germany). The obtained photocatalysts were ground in an agate mortar before photocatalytic decomposition of azo dyes and phenol.

### 2.3. Photocatalyst characterization

The photocatalysts were characterized by UV-VIS/DR technique using Jasco V-530 spectrometer (Japan) equipped with

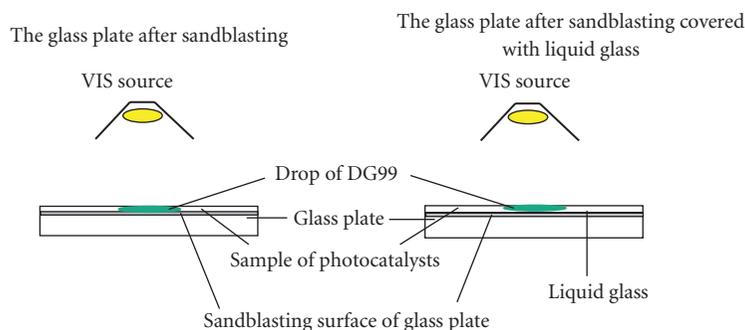


FIGURE 2: A schematic diagram of the experimental setup.

the integrating sphere accessory for diffuse reflectance spectra ( $\text{BaSO}_4$  was used as a reference).

The surface properties of the photocatalysts were examined on the basis of FTIR/DRS spectra. Measurements were performed using Jasco FTIR 430 (Japan) spectrometer equipped with a diffuse reflectance accessory (Harrick, USA).

#### 2.4. Determination of the photocatalytic activity

The photodegradation reaction was carried out in a glass reactor containing  $500 \text{ cm}^3$  of a model solution of Reactive Red 198, Direct Green 99, and phenol (initial concentrations:  $5 \text{ mg/dm}^3$ ,  $10 \text{ mg/dm}^3$ , and  $0.1 \text{ g/dm}^3$ , resp.) and  $0.2 \text{ g/dm}^3$  of a catalyst. The solution was mixed using a magnetic stirrer. After stirring in the dark for 15 minutes, the solution was following irradiation under visible light using a 100 W lamp (Philips Pila, Poland) for 5 hours in case of azo dyes and for 24 hours in case of phenol. The illumination intensity at the irradiation plate was  $354 \text{ W/m}^2$  for VIS and  $0.09 \text{ W/m}^2$  for UV range. It should be noted that the intensity of the UV radiation in the experiment was very low (0.02% of the total illumination, whereas in the solar radiation it was 5.52% at the day of the measurement). Due to this fact, the share of the UV in the irradiated light can be considered as negligible. The illumination intensities were measured with an LB 901 illumination meter equipped with the PD204AB (Macam Photometrics Ltd, Scotland) and CM3 (Dutch Office Kipp & Zonen B.V., The Netherlands) external sensors. After irradiation, the solution was filtered through a  $0.45 \mu\text{m}$  membrane filter. The concentrations of investigated compounds were determined by UV absorbance at 518 nm for Reactive Red 198, at 624 nm for Direct Green 99, and at 269 nm for phenol (Jasco V-530 spectrometer, Japan) in a 1 cm quartz cell.

#### 2.5. The photodecomposition of Direct Green 99 on the catalysts placed on the glass plate.

The photodecomposition of Direct Green 99 was carried out on  $\text{TiO}_2$ -P25 and  $\text{TiO}_2/\text{N}$  500 catalysts placed on the glass plate after sandblasting. In Figure 2, there a schematic diagram of the experimental setup is presented, where the

measurement was performed. The main component of the system was glass plate after sandblasting with or without liquid glass layer and immobilized catalyst. The cleaned and dried glass plates were coated with a sonicated water suspension of  $\text{TiO}_2$ -P25 and  $\text{TiO}_2/\text{N}$  500 (5% wt.). Such obtained glass plates with photocatalysts layer were dried in an oven at  $105^\circ\text{C}$  for 20 minutes. The azo dye Direct Green 99 was dropped onto the surface of the photocatalyst and was subjected to irradiation under artificial solar light. The concentration of a model dye on the photocatalyst surface equaled  $0.04 \text{ mg/cm}^2$ . The illumination intensity at the irradiation plate was the same as the one used for the decomposition of Direct Green 99 in a glass reactor. After every 24 hours of irradiation, the  $\text{TiO}_2/\text{N}$  500 sample coated on the glass plate was taken to UV-VIS/DR analysis. The decomposition degree of Direct Green 99 was estimated on the basis of changes in UV-VIS/DR spectra using Jasco V-530 spectrometer equipped with the integrating sphere accessory for diffuse reflectance spectra ( $\text{BaSO}_4$  was used as a reference).

### 3. RESULTS AND DISCUSSION

The UV-VIS/DR spectra of catalysts modified at different temperatures, as well as the spectrum of crude  $\text{TiO}_2$  after treatment with  $\text{NH}_{3\text{aq}}$ , are presented in Figure 3. In case of catalysts prepared at temperatures lower than  $300^\circ\text{C}$ , the only UV absorption edge ( $\lambda = 374.6 \text{ nm}$ ,  $E_G = 3.31 \text{ eV}$ ) on the UV-VIS/DR spectra is observed. With increasing the calcination temperature, the second absorption edge in the VIS region ( $\lambda \approx 470 \text{ nm}$ ,  $E_G \approx 2.64 \text{ eV}$ ) appeared. The presence of the second absorption edge could be caused by the substitutional N-doping. Asahi et al. [1] identified substitution of nitrogen in the samples with excitation of the electrons from the valence band  $\text{N}(2p_\pi)$  to the conduction band  $\text{Ti}(d_{xy})$  instead of from  $\text{O}(2p_\pi)$  as in  $\text{TiO}_2$ . At  $800^\circ\text{C}$ , a shifting of the first absorption edge to ca. 400 nm and that of the second one to ca. 483 nm ( $E_G = 2.56 \text{ eV}$ ) can be observed. The shifting of the first absorption edge is probably caused by the transformation of anatase to rutile during heat treatment at high temperature. From the presence of the additional edge in the VIS range, it can be supposed that the modified catalysts should be active under visible light illumination.

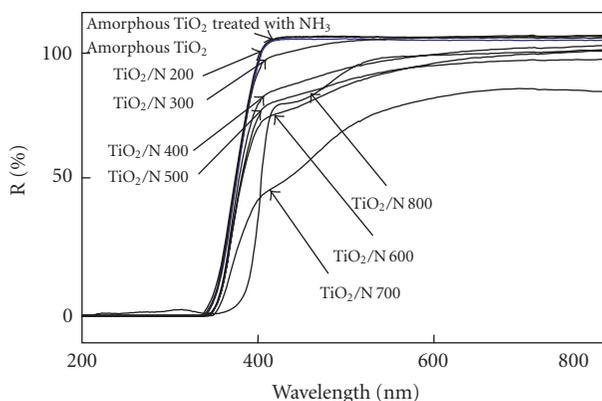


FIGURE 3: UV-VIS/DR reflection spectra of the  $\text{TiO}_2$  and  $\text{TiO}_2/\text{N}$  photocatalysts: amorphous  $\text{TiO}_2$  treated with  $\text{NH}_3$  and dried at  $100^\circ\text{C}$ ;  $\text{TiO}_2/\text{N}$  200– $\text{TiO}_2/\text{N}$  800 catalysts heated in the gaseous  $\text{NH}_3$  atmosphere at temperatures 200– $800^\circ\text{C}$ , respectively.

The decrease of the reflectance intensity with increasing the temperature of calcinations can be observed. It is probably caused by the color change of the obtained catalysts. The color of the obtained catalysts was dependent on the treatment temperature and changed with heat treatment from white (catalyst calcinated at  $100^\circ\text{C}$ ) through yellowish to vivid yellow (catalyst heated at  $800^\circ\text{C}$ ). According to Suda et al. [11], the observed tendency may be due to the concentration rate of the nitrogen atoms in the  $\text{TiO}_{2-x}\text{N}_x$  films.

The FTIR/DRS spectra of the prepared samples confirmed the presence of trace amounts of nitrogen (Mozia et al. [12]). On the FTIR spectra, some bands can be observed, the band at ca.  $1430\text{--}1440\text{ cm}^{-1}$  is attributed to the bending vibrations of  $\text{NH}_4^+$  (catalyst modified with ammonia).

The anatase/rutile ratio was estimated on the basis of XRD measurements [12–14].  $\text{TiO}_2$ -P25 consists in majority from the anatase phase (75%) and an average particle size of 30 nm. The amorphous hydrated titanium dioxide ( $\text{TiO}_2 \cdot \text{H}_2\text{O}$ ) consists from the amorphous  $\text{TiO}_2$  (67.9%), anatase (28.6%), and rutile (3.5%) phases with the crystallite sizes of 15 and 35 nm for anatase and rutile, respectively (Kosowska et al. [13]). The obtained results showed that increasing the calcination temperature resulted in transformation of amorphous  $\text{TiO}_2$  to anatase and then from anatase to rutile. The calcination temperature influenced the average size of crystallites. The crystallite size increased with increasing the temperature of calcination. The largest size of anatase and rutile crystallites was observed at  $800^\circ\text{C}$ . At the temperatures of 500– $600^\circ\text{C}$ , the ratio of the crystallite size of anatase to rutile was practically constant. The mean size of crystallites of anatase and rutile in  $\text{TiO}_2$  obtained at  $500^\circ\text{C}$  equaled 35 and 55 nm, respectively, whereas that prepared at  $600^\circ\text{C}$  equaled 45 and 65 nm, respectively. The XRD patterns of modified  $\text{TiO}_2$  did not exhibit any other diffraction peaks of new crystal phase apart from these of anatase and rutile. No nitrogen compounds (e.g.,  $\text{TiO}_{2-x}\text{N}_x$ ) were found since their content was probably too low to allow the detection by XRD method.

The photocatalytic activity of the obtained photocatalysts was investigated under visible light through the degradation

of phenol and azo dyes: Reactive Red 198 and Direct Green 99 (Figure 4). In order to determine whether the model dye and phenol solutions are resistant to degradation under VIS irradiation or not, an additional “blank” experiment without photocatalyst was performed. The batch reactor was filled with the model solution (dye or phenol) and was irradiated for 5 hours (azo dyes) and for 24 hours (phenol). After that time, the concentrations of the solutions were determined. It was found that phenol, as well as azo dyes, did not decompose under the “blank” conditions applied. Figure 4 presents the results obtained during photodegradation of phenol and dye on the N-doped photocatalysts. It can be observed that the highest effectiveness of phenol decomposition was obtained in case of catalyst calcinated at  $700^\circ\text{C}$  (6.5%) and the lowest activities for phenol degradation were found on the catalysts modified at 500, 600, and  $800^\circ\text{C}$ .

In case of degradation of both azo dyes, the highest decomposition rate was observed for catalysts calcinated at  $500^\circ\text{C}$  and  $600^\circ\text{C}$  (45% for Reactive Red 198 and 86% for Direct Green 99). The high activity of these catalysts could be explained by its phase composition (Kosowska et al. [13]). The catalyst calcinated at  $600^\circ\text{C}$  contains the crystalline phases of  $\text{TiO}_2$  (94.2% of anatase and 5.8% of rutile). In case of the catalyst heated at  $500^\circ\text{C}$ , a small amount of amorphous  $\text{TiO}_2$  (7.1%) is present, but the main phase is anatase (89.4%). A very high content of anatase results in a very low recombination of electron/hole pairs. In case of the  $\text{TiO}_2$  samples which exhibited a high photoactivity towards azo dye, a small amount of rutile still exists but with higher crystallite size. The highest activity of the  $\text{TiO}_2$  samples was noted at the optimal ratio of crystallite size of rutile to anatase – 1.5. Decrease of the activity of the samples was a result of their annealing at high temperatures between  $600^\circ\text{C}$  and  $700^\circ\text{C}$  and transformation of anatase to rutile.

It can be seen that the optimum calcination temperature of the catalysts having high activity for azo dye and phenol decomposition is different. In case of the degradation of azo dyes, the most active photocatalysts were heated at  $500^\circ\text{C}$ , whereas the highest effectiveness of phenol

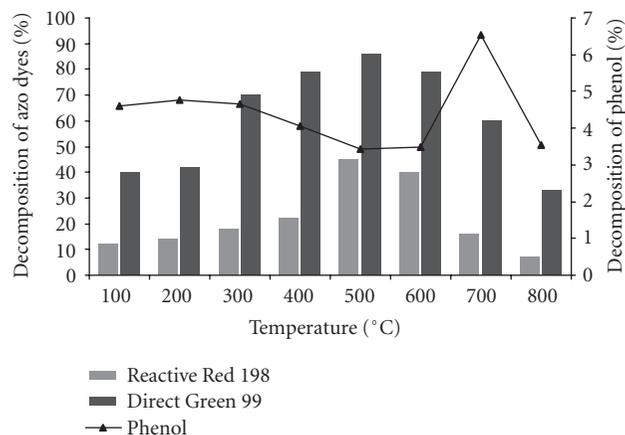


FIGURE 4: Photocatalytic decomposition of azo dyes and phenol under visible light on studied  $\text{TiO}_2/\text{N}$  sample.

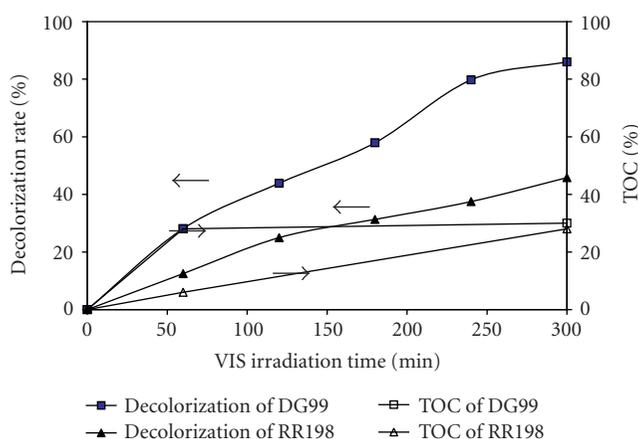


FIGURE 5: Decolorization and change of TOC of an aqueous solution of DG 99 and RR198 on  $\text{TiO}_2/\text{N}$  500 as a function of time of irradiation with visible light.

decomposition was obtained for the catalyst prepared at  $700^\circ\text{C}$ . It may result from the different mechanisms of photodegradation of dyes and other compounds, such as phenol (Kosowska et al. [13]). However, other factors, such as the crystalline structure of the photocatalysts or the effect of nitrogen doping on the photodegradation performance, should be also taken into account.

It must be emphasized that decolorization of the solution does not provide a complete data on the azo-dye degradation. Therefore, monitoring of TOC degradation should be conducted. In Figure 5, the decolorization rate and changes of TOC of an aqueous solution of DG99 and RR198 on  $\text{TiO}_2/\text{N}$  500 are shown as a function of irradiation time with visible light. After reaching the maximum of adsorption of azo dyes on  $\text{TiO}_2/\text{N}$  500, the solutions were decomposed under visible light for 5 hours. The decolorization was measured every hour, whereas TOC was carried out after adsorption and after 1 and 5 hours of photodecomposition. On the basis of changes of TOC concentration after 5 hours

of photocatalytic degradation, similar degradation rate for both azo dyes (30% for DG99 and 28% for RR198) can be observed. The photodecomposition of DG99 stopped after 1 hour and remained at the constant level, whereas RR198 was decomposed with about 6% after 1 hour and 28% after 5 hours of reaction. It can be observed that the dyes concentration decreased with time of irradiation. After 24 hours (data not shown here), the complete decolorization of both azo dyes took place. The decolorization rate was much higher than TOC removal. The prolongation of the irradiation time could probably cause the decomposition of intermediate products and improve mineralization rate.

The photodecomposition of Reactive Red 198, Direct Green 99, and phenol was carried out also on catalysts  $\text{TiO}_2\text{-P25}$ . Figure 6(a) presents the results obtained during photocatalytic decomposition of these compounds under visible light. The best decomposition results were obtained for Reactive Red 198; RR 198 removal was equal to 74%. In this case,  $\text{TiO}_2\text{-P25}$  was more active than  $\text{TiO}_2/\text{N}$  500 catalyst.

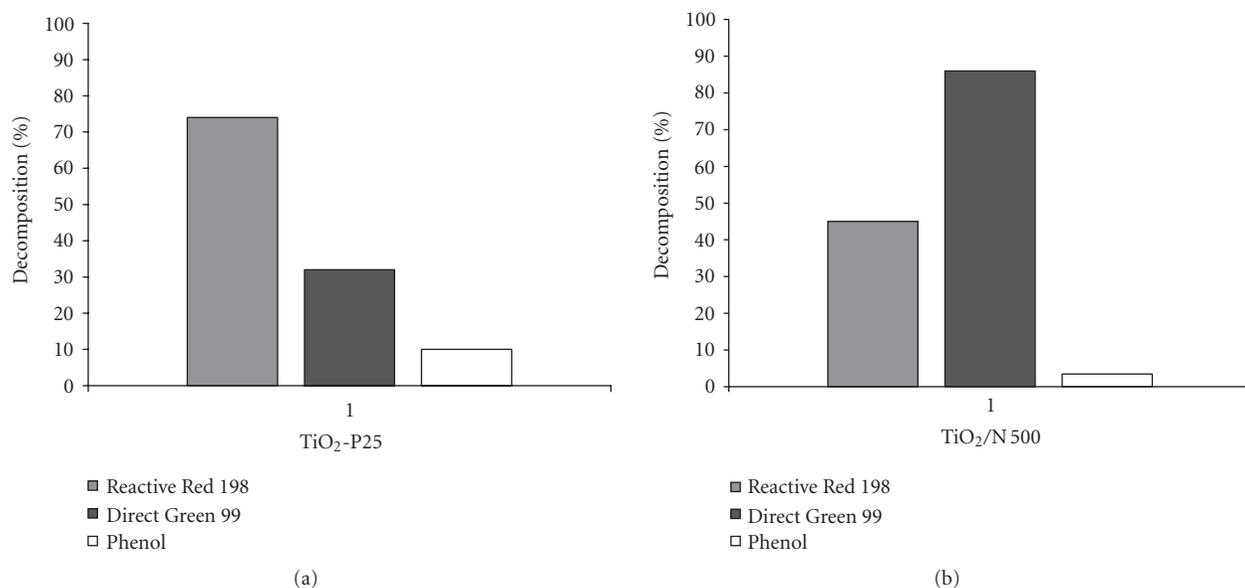


FIGURE 6: Photocatalytic decomposition of azo dyes and phenol under visible light in the slurry batch reactor ( $C_{0 \text{ Reactive Red 198}} = 5 \text{ mg/dm}^3$ ,  $C_{0 \text{ Direct Green 99}} = 10 \text{ mg/dm}^3$ ;  $C_{0 \text{ phenol}} = 0,1 \text{ g/dm}^3$ ;  $0,2 \text{ g TiO}_2/\text{dm}^3$ ) on (a) TiO<sub>2</sub>-P25 and (b) TiO<sub>2</sub>/N 500.

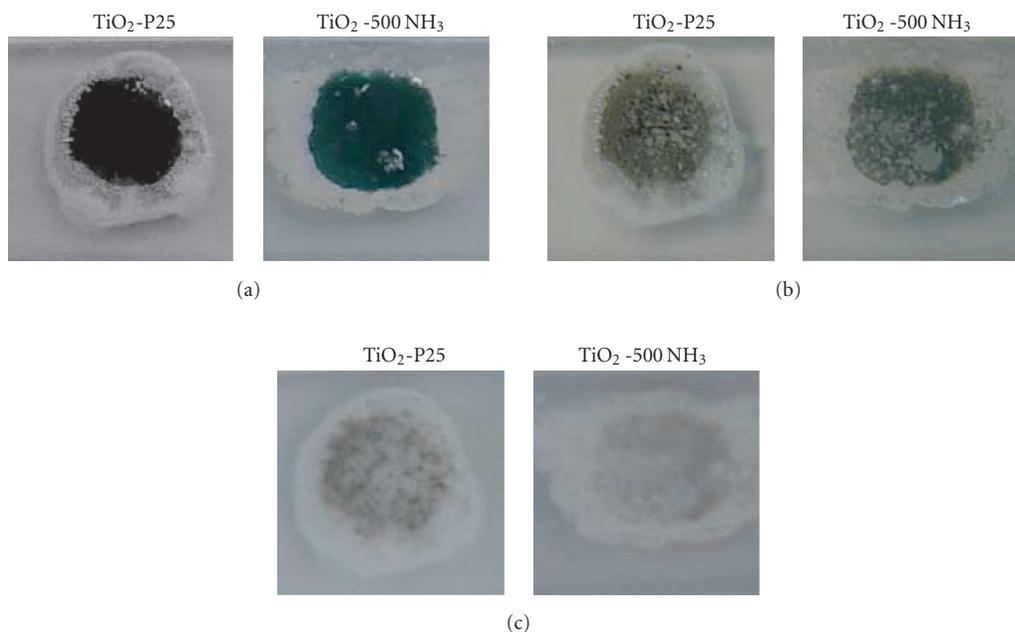


FIGURE 7: The photos of TiO<sub>2</sub>-P25 and TiO<sub>2</sub>/N 500 placed on glass plate after sandblasting with adsorbed Direct Green 99 in time of visible light irradiation (a) after drop of azo dye, (b) after 24 hours of irradiation, and (c) after 120 hours of irradiation.

It showed also higher effectiveness of photocatalytic decomposition for phenol. Phenol was degraded by 10% after 24 hours of irradiation under artificial solar light. The TiO<sub>2</sub>-P25 was less efficient for Direct Green 99 decomposition than prepared photocatalyst. Direct Green 99 was decomposed on TiO<sub>2</sub>-P25 with effectiveness of 32%, whereas on TiO<sub>2</sub>/N 500 with 86% (Figure 6(b)).

Next series of experiments were conducted in order to decompose Direct Green 99 adsorbed on the TiO<sub>2</sub>/N 500 and TiO<sub>2</sub>-P25 photocatalysts surface, which were placed on glass plate after sandblasting. In Figures 7(a)–(c), the photos of specified catalyst with adsorbed Direct Green 99 after irradiation are shown. It can be observed that in case of both catalysts, the decomposition of Direct Green 99 after

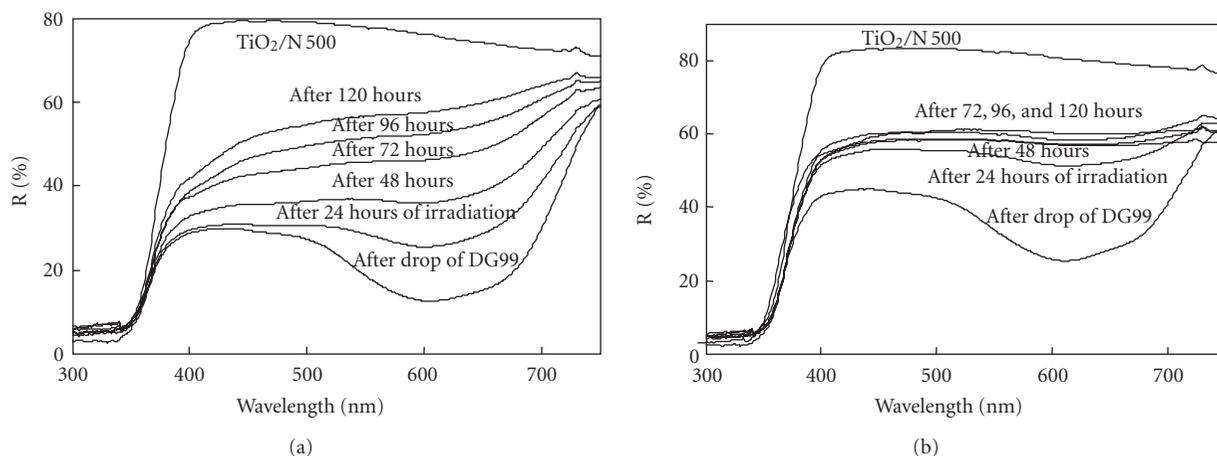


FIGURE 8: The UV-VIS/DR spectra of  $\text{TiO}_2/\text{N}$  500 catalyst placed on the glass plate after sandblasting (a) without liquid glass layer and (b) with liquid glass layer.

24 hours on the catalyst surface was the same. However after 120 hours of irradiation, the decomposition of DG 99 on  $\text{TiO}_2/\text{N}$  500 was practically complete. On  $\text{TiO}_2\text{-P25}$  surface, the process of Direct Green 99 photodegradation was not finished during 120 hours of experiment. Extending the irradiation time up to 144 hours (data not shown here), the decolorization was not complete on  $\text{TiO}_2\text{-P25}$ . The rate of decolorization of Direct Green 99 on  $\text{TiO}_2/\text{N}$  500 and  $\text{TiO}_2\text{-P25}$  equaled  $0.300 \mu\text{g} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$  and  $0.200 \mu\text{g} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ , respectively. In this case, the prepared photocatalyst showed higher photoactivity than the commercial  $\text{TiO}_2\text{-P25}$ . Our results are in accordance with literature data. Liu et al. [15] showed that the nitrogen-doped titania nanocatalysts prepared by a sol-gel method had much higher photocatalytic performance than pure  $\text{TiO}_2$  nanocrystals, and significant improvement in reactivity on  $\text{TiO}_2\text{-P25}$  particles under visible light excitation was achieved.

The next experiment was conducted with  $\text{TiO}_2/\text{N}$  500 to decompose Direct Green 99 on glass plate after sandblasting with or without liquid glass layer. Figure 8(a) presents the measurements of UV-VIS/DR spectra of used photocatalysts both after drop of azo dye on glass plate after sandblasting without liquid glass layer and after different irradiation time in comparison with spectra of pure photocatalysts. It can be observed that the drop of azo dye on the photocatalyst surface resulted in a decrease of reflectance in the spectra. For all the spectra, the decrease in the reflectance at wavelength ca. 600 nm was found, which corresponds to the absorption maximum of Direct Green 99 in the visible region. The spectrum intensity in that range becomes higher with raising the time of irradiation, indicating the decomposition of azo dye on the photocatalyst surface and regeneration of the surface of the spent samples. Above 120 hours of illumination, the spectra intensity and shape of modified photocatalyst became practically the same as in the case of the spectrum recorded for pure photocatalyst. The reproduced surface coated with photocatalyst could be used again. Figure 8(b) presents the measurements of UV-VIS/DR

spectra of used photocatalysts both after drop of azo dye on glass plate after sandblasting with liquid glass layer and after different irradiation time in comparison with spectra of pure photocatalysts. It can be observed that the drop of azo dye on the photocatalyst surface resulted in a decrease of the reflectance in the spectra, too. However the decomposition of Direct Green 99 on glass plate covered by liquid glass took place up to 24 hours of irradiation (Figure 9). The regeneration of the photocatalyst (decolorization of azo dye) was longer than in the case when liquid glass layer on the glass plate was not used. The obtained results showed that using the glass layer on the glass plate before covering with photocatalyst reduces their activity.

#### 4. CONCLUSIONS

A simple method of preparation of VIS- active photocatalysts by modification of titanium dioxide with nitrogen was presented. The amorphous hydrated titanium dioxide ( $\text{TiO}_2 \cdot \text{H}_2\text{O}$ ) obtained directly from the sulphate technology installation was doped with nitrogen by calcination at  $200\text{--}800^\circ\text{C}$  in ammonia atmosphere for 4 hours.

The nitrogen doping during calcinations under ammonia atmosphere is a new way of obtaining a photocatalyst which could have a practical application in water treatment system under broadened solar light spectrum.

The prepared photocatalyst showed higher photoactivity than the commercial  $\text{TiO}_2\text{-P25}$  for decolorization Direct Green 99.

Mineralization degree followed the decolorization rate, however it was much lower than it should be expected from the disappearance of color, because of the formation of the no-colored intermediates.

The mentioned deposition of the catalyst on the glass exhibited high activity and also self-cleaning properties with high reproducibility.

The glass layer on glass plate before cover with photocatalyst reduced its photoactivity on azo-dyes decolorization.

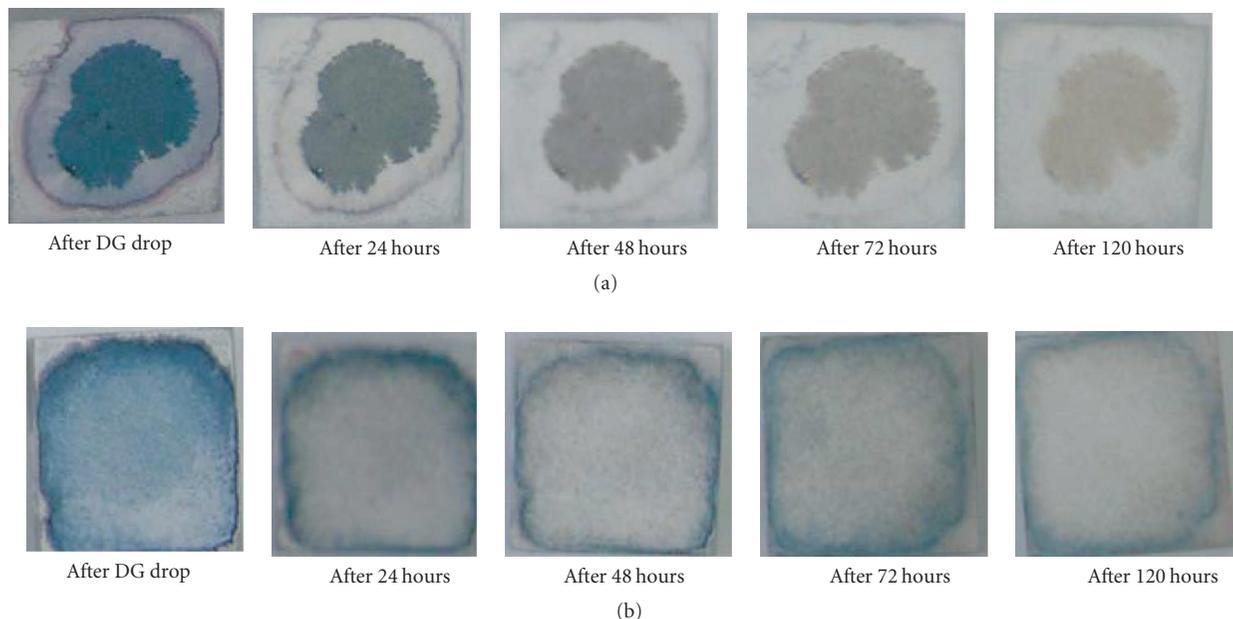


FIGURE 9: The photos of  $\text{TiO}_2/\text{N}$  500 placed on glass plate after sandblasting with adsorbed Direct Green 99 in time of visible light irradiation (a) without liquid glass layer and (b) with liquid glass layer.

## ACKNOWLEDGMENT

This work was supported by the Research Project PBZ-KBN-116/T09/2004 for 2005–2008.

## REFERENCES

- [1] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides," *Science*, vol. 293, no. 5528, pp. 269–271, 2001.
- [2] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides," *R & D Review of Toyota CRDL*, vol. 36, no. 3, p. 6, 2001.
- [3] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, and S. Sugihara, "Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping," *Applied Catalysis B: Environmental*, vol. 42, no. 4, pp. 403–409, 2003.
- [4] M. Styliidi, D. I. Kondarides, and X. E. Verykios, "Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous  $\text{TiO}_2$  suspensions," *Applied Catalysis B: Environmental*, vol. 40, no. 4, pp. 271–286, 2003.
- [5] W. S. Kuo and P. H. Ho, "Solar photocatalytic decolorization of methylene blue in water," *Chemosphere*, vol. 45, no. 1, pp. 77–83, 2001.
- [6] C. Burda, Y. Lou, X. Chen, A. C. S. Samia, J. Stout, and J. L. Gole, "Enhanced nitrogen doping in  $\text{TiO}_2$  nanoparticles," *Nano Letters*, vol. 3, no. 8, pp. 1049–1051, 2003.
- [7] J. L. Gole, J. D. Stout, C. Burda, Y. Lou, and X. Chen, "Highly efficient formation of visible light tunable  $\text{TiO}_{2-x}\text{N}_x$  photocatalysts and their transformation at the nanoscale," *Journal of Physical Chemistry B*, vol. 108, no. 4, pp. 1230–1240, 2004.
- [8] Y. Wang, "Solar photocatalytic degradation of eight commercial dyes in  $\text{TiO}_2$  suspension," *Water Research*, vol. 34, no. 3, pp. 990–994, 2000.
- [9] C. Guillard, J. Disdier, J.-M. Herrmann, et al., "Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol," *Catalysis Today*, vol. 54, no. 2-3, pp. 217–228, 1999.
- [10] J.-M. Herrmann, C. Guillard, J. Disdier, C. Lehaut, S. Malato, and J. Blanco, "New industrial titania photocatalysts for the solar detoxification of water containing various pollutants," *Applied Catalysis B: Environmental*, vol. 35, no. 4, pp. 281–294, 2002.
- [11] Y. Suda, H. Kawasaki, T. Ueda, and T. Ohshima, "Preparation of high quality nitrogen doped  $\text{TiO}_2$  thin film as a photocatalyst using a pulsed laser deposition method," *Thin Solid Films*, vol. 453-454, pp. 162–166, 2004.
- [12] S. Mozia, M. Tomaszewska, B. Kosowska, B. Grzmil, A. W. Morawski, and K. Kafucki, "Decomposition of nonionic surfactant on a nitrogen-doped photocatalyst under visible-light irradiation," *Applied Catalysis B: Environmental*, vol. 55, no. 3, pp. 195–200, 2005.
- [13] B. Kosowska, S. Mozia, A. W. Morawski, B. Grzmil, M. Janus, and K. Kafucki, "The preparation of  $\text{TiO}_2 \cdot x\text{H}_2\text{O}$  under ammonia atmosphere for visible light photocatalysis," *Solar Energy Materials and Solar Cells*, vol. 88, no. 3, pp. 269–280, 2005.
- [14] B. Wawrzyniak and A. W. Morawski, "Solar-light-induced photocatalytic decomposition of two azo dyes on new  $\text{TiO}_2$  photocatalyst containing nitrogen," *Applied Catalysis B: Environmental*, vol. 62, no. 1-2, pp. 150–158, 2006.
- [15] Y. Liu, X. Chen, J. Li, and C. Burda, "Photocatalytic degradation of azo dyes by nitrogen-doped  $\text{TiO}_2$  nanocatalysts," *Chemosphere*, vol. 61, no. 1, pp. 11–18, 2005.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

