Adriana Zaleska*

CHARACTERISTICS OF DOPED-TiO$_2$
PHOTOCATALYSTS

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Titanium dioxide represents an effective photocatalyst for water and air purification and for self-cleaning surfaces. TiO$_2$ shows relatively high reactivity and chemical stability under ultraviolet light ($\lambda<$387nm), whose energy exceeds the band gap of 3.3 eV in the anatase crystalline phase. The development of photocatalysts exhibiting high reactivity under visible light ($\lambda>380$nm) should allow the main part of the solar spectrum, even under poor illumination of interior lighting, to be used. In this work the influence of TiO$_2$ structure on visible light photoactivity and novel photocatalysts doped with sulfur, nitrogen, boron and carbon are presented. The photocatalytic activity of obtained powders was referred to dopant chemical form, crystalline structure, crystallite size, surface area and preparation method.

key words: doped-TiO$_2$, heterogeneous photocatalysis, visible light-driven photocatalysis

INTRODUCTION

Titanium dioxide has semi-conducting properties which make it an attractive material to be used as a photoactive catalyst. TiO$_2$ is widely used for air purification, deodorization, sterilization, anti-fouling, and mist removal (Fujishima and Zhang, 2006). Activity of TiO$_2$ depends on its surface area, porosity and acid-basic properties. It was also found that the photoactivity depends on the crystallite size and relative abundance of the crystalline phases (anatase/rutile). Both the crystallite size and crystalline phases modify the TiO$_2$ band gap. The pristine TiO$_2$ is only active upon ultraviolet light ($\lambda<387$ nm) because of its band gap (3.2 eV in the anatase TiO$_2$ crystalline phase). To improve the photocatalytic reactivity of TiO$_2$ and to extend its light ab-
Both approaches introduce impurity/defect states in the band gap of TiO$_2$, which lead TiO$_2$ to absorb visible-light. However, transition metal doping, where quite local---
ized \(d\) states appear deep in the band gap of the host semiconductor, often results in the increase of the carrier recombination. Therefore, the lifetime of the mobile carriers may become shorter, giving lower photocatalytic activity. Reducing \(\text{TiO}_2\) introduces localized oxygen vacancy states located at 0.75-1.18 eV below the conduction band (CBM) of \(\text{TiO}_2\), which may promote photoreduction activity because a redox potential of the hydrogen evolution (\(\text{H}_2/\text{H}_2\text{O}\)) locates just below the CBM of \(\text{TiO}_2\). In 2001, Asahi et al., presented a new type of visible light sensitive photocatalyst - nitrogen-doped \(\text{TiO}_2\). Since Asahi paper, other non-metal doped \(\text{TiO}_2\) photocatalysts were reported. \(\text{TiO}_2\) doped with F (Yu et al, 2002), I (Hong et al., 2005) and P (Yu et al., 2003) showed higher photocatalytic activity under UV light and \(\text{TiO}_2\) doped with N (Irie et al., 2003a; Asahi et al., 2007), C (Sakthivel and Kisch, 2003), S (Ohno et al., 2003) and codoped with Ni and B (Zhao et al., 2004) showed high photocatalytic activity under visible light. Sato et al.,(2005) have shown efficient photooxidation of CO under visible irradiation by a nitrogen-doped \(\text{TiO}_2\). C-doped \(\text{TiO}_2\) was obtained by acid-catalyzed sol-gel process (Lettmann et al., 2001) or by the oxidative annealing of \(\text{TiC}\) (Irie et al.,2003b). Examples of doping methods and selected properties of non-metal doped-\(\text{TiO}_2\) are given in Table 1.

Non-metal doping opens up a new possibility for the development of solar- or daylight-induced photocatalytic materials. In the present work, several own nonmetal-doped photocatalysts are presented: C-doped, B,C codoped and S,N,C-tridoped \(\text{TiO}_2\). The selected properties of the obtained photocatalysts were correlated with their photoactivity under visible light. Their intrinsic characteristics were investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-Vis spectroscopy. The photocatalytic activity of doped \(\text{TiO}_2\) was evaluated by the degradation rate of phenol.

**METHODS**

**PREPARATION OF NONMETAL-DOPED \(\text{TiO}_2\) PHOTOCATALYSTS**

C-doped \(\text{TiO}_2\) was prepared by titanium(IV) isopropoxide (TIP, 97\%, Sigma-Aldrich Co.) hydrolysis, followed by precipitate separation, drying at 80°C for 24 h and calcinations at 350°C for 1 h. Low calcination temperature favors to keep residual carbon in photocatalyst structure. Carbon comes from alkoxide \(\text{TiO}_2\) precursor. B, C-codoped \(\text{TiO}_2\) was obtained by sol-gel method (H-labeled) and by grinding anatase with boron precursors (G-labeled). Boric acid triethyl ester (99\%) and boric acid (99\%) from Sigma-Aldrich Co) were used as a boron source in both procedures. In sol-gel method, TIP was hydrolyzed in the presence of appropriate dopant, followed by precipitate separation, drying at 80°C for 24 h and calcinations at 450°C for 1 h. Titanium dioxide ST-01 from Ishihara-Sangyo, Japan, was used in the second proce-
dure. ST-01 has 320 m²/g specific surface area and consists only of crystalline anatase phase with 7 nm particle size. Boron-modified TiO₂ powders were prepared by grinding ST-01 in agate mortar with H₃BO₃ or (C₂H₅O)₃B, respectively. The obtained powders were dried for 24 h at temperature 80ºC and calcinated at 450ºC.

S, N, C-tridoped photocatalysts were obtained by sol-gel method. Thioacetamide (99%) from POCH S.A. and thiourea (99%) from Sigma-Aldrich Co. were used as sulfur and nitrogen source in catalyst preparation procedures. TIP was hydrolyzed in the presence of appropriate dopant, followed by precipitate separation, drying at 80ºC for 24 h and calcinations at 450ºC for 1 h. The detailed experimental procedure can be found in previous studies (Zaleska et al., 2007; Zaleska et al., 2008; Górska et al., 2008).

CHARACTERIZATION

ESCALAB-210 spectrometer (VG Scientific) was used for X-ray photoelectron spectroscopy (XPS) measurements with the Al Kα X-ray source operated at 300W (15kV, 20mA). The spectrometer chamber pressure was about 5×10⁻⁹ mbar. The survey spectra were recorded for all the samples in the energy range from 0 to 1350 eV with 0.4 eV step. High resolution spectra were recorded with 0.1 eV step, 100 ms dwell time and 20 eV pass energy. 90° take-off angle was used in all measurements. AVANTAGE data system software served for curve fitting. The background was fit using nonlinear Shirley model. Scofield sensitivity factors and measured transmission function were used for quantification. Carbon contamination C1s peak at 284.60 eV was used as reference of binding energy. The catalyst powder crystal structure was determined from XRD pattern measured in the range of 2 θ=20÷80º using X-ray diffractometer (Xpert PRO-MPD, Philips) with Cu target Kα-ray (λ=1.5404 Å). The diffuse absorption spectra DRS were characterized using UV-VIS spectrometer (Jasco, V-530) equipped with an integrating sphere accessory for diffuse reflectance.

ASAP 2405 instrument (Micromeritics) was used for measurements of BET surface area and pore size of the catalysts by physical adsorption and desorption of nitrogen. The S_BET values were calculated according to the BET method using adsorption data at relative pressures p/p₀ between 0.05 and 0.25, where p and p₀ denote the equilibrium pressure. Mesopore-size distribution was calculated with the Barrett-Joyner-Halenda method of isotherm.

MEASUREMENT OF PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of doped-TiO₂ powders in visible light (λ > 400 nm) was estimated by measuring the decomposition rate of phenol (0.21 mmol/dm³) in an aqueous solution. Photocatalytic degradation runs were proceeded with blind tests in the absence of catalyst or illumination.
25 cm$^3$ of catalyst suspension (125 mg) was stirred using magnetic stirrer and aerated (5 dm$^3$/h) prior and during the photocatalytic process. Aliquots of 1.0 cm$^3$ of the aqueous suspension were collected at regular time periods during irradiation and filtered through syringe filters (Ø=0.2 µm) to remove catalyst particles. Phenol concentration was estimated by colorimetric method using UV-VIS spectrophotometer (DU-7, Beckman). The suspension was irradiated using 1000 W Xenon lamp (Oriel), which emits both UV and Vis light. To limit the irradiation wavelength, the light beam was passed through GG400 to cut-off wavelengths shorter than 400 nm.

RESULTS AND DISCUSSION

The selected properties of nonmetal-doped photocatalysts and pure TiO$_2$ as a reference sample are given in Table 2. Phenol degradation rate was calculated as an average phenol amount removal after 60 min. visible light illumination. It was observed, that C-doped TiO$_2$ (sample T_350 obtained by TIP hydrolysis without any dopant and calcination at 350°C) revealed similar photoactivity to S,N,C-tridoped TiO$_2$ (sample TH_5 obtained by modification with thiourea). Phenol degradation rate under visible light was 2.93 and 2.82 µmol·dm$^{-3}$·min$^{-1}$ for TH_5 and T_350, respectively. For pure TiO$_2$ the observed phenol degradation ranged from 0.6 (TiO$_2$ prepared by sol-gel method) to 0.9 µmol·dm$^{-3}$·min$^{-1}$ (commercially available TiO$_2$ ST01).

The obtained results suggested that visible-light-activated TiO$_2$ could be prepared by carbon, sulfur, nitrogen or boron doping or co-doping of those moieties. For TiO$_2$ modified with thiourea, thiourea or boric acid triethyl ester, phenol degradation rate exceeded 2 µmol·dm$^{-3}$·min$^{-1}$.

XRD was used to investigate the phase structure of nonmetal-doped TiO$_2$ powders (see data on crystalline phase in Table 2). For all highly-active C-doped and S,N,C-tridoped photocatalysts a homogenous crystalline phase of anatase appeared in the XRD pattern. B,C-codoped TiO$_2$ obtained by the sol-gel method, except the sample BA-H(0.5), appeared as amorphous TiO$_2$, while pure TiO$_2$ obtained by the same method without any dopant was in the anatase form. Addition of (C$_2$H$_5$O)$_3$B or H$_3$BO$_3$ inhibited crystallite growth and/or transformation from amorphous to anatase structure. Only addition of the smallest amount of H$_3$BO$_3$ (0.5 wt.%), resulted in anatase structure (Table 2).

All samples obtained by grinding of ST-01 with boron compounds still contained the anatase phase. The XRD pattern of samples BA-G(10) and BE-G(10) shows diffraction lines attributed to the diboron trioxide phase besides the peak due to anatase. Chen et al.,(2006) found that appearance of separate boron phase is related not only to the calcination temperature but also the molar ratio of B to Ti. For samples with molar ratio Ti : B =10 the diboron trioxide crystal appeared during calcination over 600°C. When Ti : B was 20, the B$_2$O$_3$ phase emerged at 500°C. In our study, B$_2$O$_3$ structure
was observed for samples prepared by grinding with 10 wt.% of boron in two different precursors. Apparently 0.5 wt.% was not enough to form clearly evident $\text{B}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>Doping moiety</th>
<th>Sample name*</th>
<th>Dopant precursor**</th>
<th>Dopant amount [wt. %]</th>
<th>Calcination temperature [°C]</th>
<th>Phase composition</th>
<th>Band gap energy [eV]</th>
<th>Phenol decomposition reaction rate [$\mu$mol·dm$^{-3}$·min$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S, N, C</td>
<td>TA0.5 thioacetamide</td>
<td>0.5</td>
<td>450</td>
<td>anatase</td>
<td>3.37</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TA1 thioacetamide</td>
<td>1.0</td>
<td>450</td>
<td>anatase</td>
<td>3.36</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TA2 thioacetamide</td>
<td>2.0</td>
<td>450</td>
<td>anatase</td>
<td>3.36</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TA5 thioacetamide</td>
<td>5.0</td>
<td>450</td>
<td>anatase</td>
<td>3.36</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TH0.5 thiourea</td>
<td>0.5</td>
<td>450</td>
<td>anatase</td>
<td>3.34</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TH1 thiourea</td>
<td>1.0</td>
<td>450</td>
<td>anatase</td>
<td>3.33</td>
<td>1.2</td>
<td></td>
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<tr>
<td></td>
<td>TH2 thiourea</td>
<td>2.0</td>
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<td>anatase</td>
<td>3.37</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TH5 thiourea</td>
<td>5.0</td>
<td>450</td>
<td>anatase</td>
<td>3.37</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>B, C</td>
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<td>450</td>
<td>amorphous</td>
<td>3.28</td>
<td>0.5</td>
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<tr>
<td></td>
<td>BE-H(1) BATE</td>
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<td>450</td>
<td>amorphous</td>
<td>3.37</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>amorphous</td>
<td>3.41</td>
<td>0.5</td>
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<tr>
<td></td>
<td>BE-H(10) BATE</td>
<td>10.0</td>
<td>450</td>
<td>amorphous</td>
<td>3.36</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BE-G(0.5) BATE</td>
<td>0.5</td>
<td>450</td>
<td>anatase</td>
<td>3.36</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BE-G(10) BATE</td>
<td>10.0</td>
<td>450</td>
<td>anatase + $\text{B}_2\text{O}_3$</td>
<td>3.37</td>
<td>1.4</td>
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<td></td>
<td>BA-H(0.5) boric acid</td>
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<td>450</td>
<td>anatase</td>
<td>3.34</td>
<td>0.6</td>
<td></td>
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<tr>
<td></td>
<td>BA-H(10) boric acid</td>
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<td>450</td>
<td>amorphous</td>
<td>3.40</td>
<td>0.9</td>
<td></td>
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<tr>
<td></td>
<td>BA-G(0.5) boric acid</td>
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<td>450</td>
<td>anatase</td>
<td>3.30</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BA-G(10) boric acid</td>
<td>10.0</td>
<td>450</td>
<td>anatase + $\text{B}_2\text{O}_3$</td>
<td>3.33</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>T_350 no dopant</td>
<td>-</td>
<td>350</td>
<td>anatase</td>
<td>3.41</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T_450 no dopant</td>
<td>-</td>
<td>450</td>
<td>anatase</td>
<td>3.33</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ ST-01 no dopant</td>
<td>-</td>
<td>450</td>
<td>anatase</td>
<td>3.30</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

* TA, TH, BE-H and BA-H series – prepared by TIP hydrolysis in the presence of an appropriate dopant; BE-G and BA-G series – prepared by grinding of ST01 with an appropriate dopant

** BATE - boric acid triethyl ester

The band gap for doped-TiO$_2$ fluctuated from 3.28 to 3.41 eV. The highest $\varepsilon_g$ was observed for highly active C-doped TiO$_2$ (sample T_350 obtained by TIP hydrolysis followed by calcination at 350°) and inactive B,C-codoped TiO$_2$ (sample BE-H(5) prepared by sol-gel method using 5 wt.% of boric acid triethyl ester), see Table 2. Band gap narrowing has not been observed in case of any nonmetal-doped TiO$_2$, which is in good agreement with theoretical calculation made by Xu et al.,(2006), but contrary to Asahi et al.,(2001) hypothesis. Asahi et al.,(2001) postulated band gap narrowing as the main modification mechanism of TiO$_2$ doped with nonmetals.
Characteristics of doped-TiO$_2$ photocatalysts

Usually, nonmetal doping affects light absorption characteristics of TiO$_2$. Figure 1 shows the UV-vis diffuse reflectance spectra of pure TiO$_2$, S,N,C-tridoped TiO$_2$ (Fig. 1A) and B,C-codoped TiO$_2$ (Fig. 1B). All nonmetal-doped TiO$_2$ powders better absorbed visible light, however, the red shift is negligible. Photoabsorption in the visible region was stronger for TiO$_2$ doped with S, N, B or C atoms than for pure TiO$_2$ (Fig. 1). Only for S,N,C-tridoped TiO$_2$ clear correlation between absorption spectra and photoactivity was observed, i.e. for increased photoactivity absorption in visible region also increased (reflectance decreased).

To investigate the chemical states of nonmetals atoms incorporated into TiO$_2$ binding energies were measured by X-ray photoemission spectroscopy. Table 3 shows chemical content, as well as phenol degradation efficiency under visible light, for selected – the most active photocatalysts. Photocatalysts are listed from higher to lower photoactivity. In all doped-TiO$_2$ samples the peak attributed to C 1s at around 289-284 eV was observed. In most cases, the C 1s region consists of three peaks: the first peak (~288.9 eV) related to COOH groups bonds, the second peak (~286 eV) to C-OH bonds and the third peak (~284.6 eV) related to C-C aromatic bonds. Thus, carbon content is presented as a total C content, C-C structure (both C-C$_{alif}$ and C-C$_{arom}$) and as carbon in form of C-C$_{arom}$. All visible-light-activated photocatalysts contain carbon including carbon in the form of C-C$_{arom}$.

![Fig. 1. Diffuse reflectance spectra of pure and doped-TiO$_2$: (A) S,N,C-tridoped TiO$_2$ prepared by hydrolysis of TIP in the presence of thiourea, (B) B,C-codoped TiO$_2$ prepared by hydrolysis of TIP in the presence of $(C_2H_5O)_3B$](image)

Among all obtained powders, the highest visible-light activity was observed for the S,N,C-tridoped TiO$_2$ - prepared with 5 wt.% of thiourea. The rate constant for phenol and 4-chlorophenol decomposition was 0.054 and 0.041 min$^{-1}$, respectively. The most effective catalyst contained 1.3 at.% of nitrogen, 7.21 at.% of carbon and 0.33 at. % of sulfur, as indicated by XPS analysis. TH5 sample is one of the richest in sulfur (Table 3), mainly in S$^{6+}$ species. On the other hand, TH5 carbon content remained in medium range.
High visible-light activity was also observed for C-doped TiO$_2$, containing residual carbon from organic titanium dioxide precursor. Since surface area and pore size distribution are important factors for heterogeneous photocatalysis, the sample T$_{350}$ had high BET surface area (205.8 m$^2$/g) and small crystallite size (8.4 nm) and average pore diameter (8.3 nm). Enhanced visible light activity probably results from the presence of carbon (15.2 at.%), mainly in the form of C-C species, as well as from high surface area. Although, there is no red shift observed for sample T$_{350}$, it exhibited better light absorption in Vis – moreover, the absorption tail was extended to 750 nm.

According to Sakthivel and Kisch (2001) hypothesis, there is an optimal amount of dopant responsible for enhanced visible light activity. Besides the dopant amount, the chemical character of incorporated element is also important. Literature data and obtained results suggested that carbon in the form of carbonate and boron as boron trioxide suppress visible-light activity. Lettmann et al.,(2001), as well as Umebayashi et al,(2003) stated that carbon species works as sensitizer and single oxygen is formed without TiO$_2$ excitation. Yu and co-workers (2005) provided an alternative explanation that sulfur doping can indeed create intra-band gap states close to the conduction band edges, and thus induces visible-light absorption at the sub-band energy. It was also found, that constitution of the TiO$_2$ (doped and undoped TiO$_2$) also plays an important role in its high photoactivity (Yu et al., 2006). Usually, the composite of two kinds of semiconductor or two phases of the same semiconductor is beneficial in reducing the recombination of photo-generated electrons and holes, and thus enhances photocatalytic activity. The interface between the two phases may act as a rapid separation site for the photo-generated electrons and holes due to the difference in the energy level of their conduction bands and valence bands. Therefore, Yu et al.,(2006) suggested that N,S-codoped TiO$_2$ powders prepared by hydrolysis method exhibit significant photoactivity under daylight illumination due to the fact that the as-prepared TiO$_2$ powders consist of two phases of undoped TiO$_2$ and N,S-codoped TiO$_2$. 

### Table 3. Chemical characterization of most visible light activated TiO$_2$ photocatalysts

<table>
<thead>
<tr>
<th>Sample No</th>
<th>ΣC</th>
<th>C-C</th>
<th>C-C arom</th>
<th>S</th>
<th>N</th>
<th>B</th>
<th>Phenol degradation efficiency after 60 min. irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH 5</td>
<td>7.21</td>
<td>3.69</td>
<td>1.71</td>
<td>0.33</td>
<td>1.3</td>
<td>-</td>
<td>97</td>
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<tr>
<td>T 350</td>
<td>15.2</td>
<td>10.1</td>
<td>10.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>82</td>
</tr>
<tr>
<td>TH 2</td>
<td>14.89</td>
<td>9.86</td>
<td>9.86</td>
<td>0.33</td>
<td>1.15</td>
<td>-</td>
<td>82</td>
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<tr>
<td>TA 5</td>
<td>6.37</td>
<td>4.95</td>
<td>2.76</td>
<td>0.16</td>
<td>1.24</td>
<td>-</td>
<td>81</td>
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<tr>
<td>TA 2</td>
<td>2.52</td>
<td>1.5</td>
<td>0.83</td>
<td>-</td>
<td>1.21</td>
<td>-</td>
<td>72</td>
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<tr>
<td>BE-G(0.5)</td>
<td>18.54</td>
<td>12.77</td>
<td>12.77</td>
<td>-</td>
<td>-</td>
<td>3.21</td>
<td>61</td>
</tr>
<tr>
<td>BE-G(10)</td>
<td>18.43</td>
<td>9.55</td>
<td>9.55</td>
<td>-</td>
<td>-</td>
<td>12.33</td>
<td>45</td>
</tr>
</tbody>
</table>
CONCLUSION

1. Using several new dopants, a series of TiO₂ catalyst samples was selected for investigation aimed at correlation of their structure and photoactivity. Particularly S,N,C-tridoped (obtained by TIP hydrolysis in the presence of thioacetamide and thermal treating at 450°C) and C-doped (obtained by TIP hydrolysis in the absence of any dopant and thermal treating at 350°C) photocatalysts were active under visible light at wavelengths greater than 400 nm.
2. B³⁺, S⁺ and carbon in the form of C-aromatic species showed beneficial influence on photodegradation efficiency in visible light.
3. For S,N,C-tridoped photocatalysts, the experimental data clearly indicate the presence of correlation between absorption and photoactivity of the obtained powders - for increased photoactivity absorption in visible region also increased.
4. The experimental data confirm earlier observations, that a lack of band gap narrowing with simultaneous increase of the absorption intensity can still lead to effective degradation of the organic compounds, which is mainly controlled by presence of sensitizers (residual carbon).

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REFERENCES


Fotokatalityczne właściwości TiO$_2$ wykorzystywane są między innymi do eliminacji substancji organicznych z fazy gazowej i ciekłej oraz w samooczyszczaniu powierzchni. Tlenek tytanu (IV) absorbuje prawie wyłącznie promieniowanie UV, dlatego podczas fotokatalizy wykorzystać można zaledwie od 3 do 5 % promieniowania słonecznego. Zatem otrzymanie półprzewodnika tytanowego nowej generacji aktywnego w zakresie promieniowania widzialnego ($\lambda>$400 nm), znacząco rozszerzyłoby możliwości aplikacyjne fotokatalizy heterogenicznej w ochronie środowiska, przez wykorzystanie głównej części spektrum światła słonecznego lub zastosowanie źródła światła o mniejszym natężeniu promieniowania.

W niniejszej pracy omówiono nowe fotokatalizatory aktywne pod wpływem światła widzialnego, otrzymane poprzez modyfikację TiO$_2$ związkami siarki, azotu, boru oraz węgla. Fotoaktywność otrzymanych fotokatalizatorów została odniesiona do charakteru chemicznego wprowadzonej domieszkii, struktury krystalicznej, wielkości krystalitów, powierzchni właściwej fotokatalizatora oraz metody otrzymywania.

Słowa kluczowe: półprzewodnik-TiO$_2$, fotokataliza heterogeniczna, fotokatalizatory aktywne pod wpływem światła widzialnego