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Structural, morphological, and optical study of titania-based nanopowders suitable for photocatalytic applications

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Abstract. Systematic investigation of the relationship between structural, morphological, optical and photocatalytic properties of the titania-based nanopowders is presented. A series of pure and doped titania catalysts with various (anatase and brookite) phase compositions have been prepared by sol–gel or hydrothermal route. The crystal structure and composition of the synthesized samples have been extensively characterised by XRD and Raman scattering measurements. The nanopowder morphology has been studied using microscopic methods (SEM, AFM, and STM), whereas the porous structure has been revealed by the analysis of nitrogen sorption data. The optical and electronic properties have been studied by spectroscopic ellipsometry. All investigated properties have been correlated to photocatalytic activity, tested in degradation of the pharmaceutically active substances (such as metoprolol and alprazolam) induced by UVA or visible radiation. Based on this correlation, the physical properties which contribute most to the increase in photocatalytic activity of synthesized nanopowders have been determined, in order to optimize the synthesis conditions which could lead to the maximal efficiency in degradation of particular pollutant.

1. Introduction
Titanium dioxide (titania, TiO2) is known as a polymorphic material with three naturally occurring crystalline modifications (anatase, rutile, and brookite), composed of TiO6 octahedra sharing the edges and corners in a different manners [1]. As environmentally-friendly material, titania with various content of these polymorphs has been recognized as the most promising photocatalyst suitable for decomposition of various organic pollutants in the water and air. The possibility to improve photocatalytic performance of porous TiO2 nanocrystalline powders by changing the synthesis conditions, as well as doping with different ions (usually the transition metals and rare earth elements) attracted extensive attention in recent decades. More than 16,000 publications indexed in the Web of Science database have been devoted to the photocatalysts based on TiO2 (and/or comparison of the photocatalytic efficiency of some other catalysts to the efficiency of TiO2) in the last 15 years, with continuous growth in the number of publications per year (figure 1). In spite of such a large number of publications, targeted modification of the TiO2 properties (such as content, crystallinity and stoichiometry of different TiO2 phases; crystallite size and micro strain; specific surface area, pore size distribution, shape and complexity; energy of band gap; the type and amount of surface O–H groups
which may be crucial for improving its photocatalytic efficiency in degradation of some specific pollutants still requires further research.

Among a large number of pollutants, the influence of pharmaceuticals is considered as an emerging environmental problem, due to long term usage worldwide. Namely, continuous input and persistence of human and veterinary medicinal compounds to the aqueous system, even at low concentrations, may result in a potential risk for aquatic and terrestrial organisms. For all of these reasons, our recent research has been focused on the modification of the structural, compositional, morphological, surface, electronic and optical properties of TiO\textsubscript{2} nanopowders by changing synthesis and doping conditions, tailored to improve photocatalytic efficiency of TiO\textsubscript{2} in degradation of two pharmaceuticals, metoprolol and alprazolam.

According to the literature, β-blocker metoprolol tartrate salt, a cardiovascular drug known among most frequently detected pharmaceuticals in wastewaters, is listed in concentration of 10\textsuperscript{-3}–390 ng L\textsuperscript{-1} [3]. Alprazolam is one of the 5\textsuperscript{th} generation benzodiazepines, a group of psychiatric substances acting on the central nervous system [4], occurring in the environment in the range of ng L\textsuperscript{-1}–µg L\textsuperscript{-1} [5]. Although in trace concentrations, the presence of those pharmaceuticals in the environment is considered potentially dangerous, as they are persistent against biological degradation, retaining their chemical structure long enough [6]. To obtain photocatalyst efficient enough in comparison to commercial titania Degussa P25 (with anatase to rutile phase ratio of about 80:20) in MET degradation under UVA light irradiation we have synthesized anatase TiO\textsubscript{2} nanopowders by sol-gel route with several synthesis parameters varied [2, 7]. The La-doped anatase TiO\textsubscript{2} nanopowders have also been synthesized via sol–gel route [8], to study the influence of doping on TiO\textsubscript{2} efficiency in MET degradation. The brookite type TiO\textsubscript{2} nanopowders have been prepared by combination of sol–gel and hydrothermal methods and their activity in photocatalytic degradation of alprazolam has been investigated and compared to the activity of Degussa P25 [9]. Several characterization techniques (including the X-ray diffraction (XRD), scanning electron microscopy (SEM), non-contact atomic force microscopy (nc-AFM), scanning tunnelling microscopy and spectroscopy (STM/STS), energy dispersive X-ray spectroscopy (EDS), nitrogen physisorption measurements, Fourier transform infrared (FTIR) and Raman spectroscopy, spectroscopic ellipsometry (SE)) have been employed to correlate structural, morphological, surface, electronic and optical properties of synthesized TiO\textsubscript{2} nanopowders with their photocatalytic activity under ultraviolet (UVA) irradiation. The experimental details related to the applied techniques and photocatalytic measurements, can be found in our previous papers [2, 7-9].

2. Improving the efficiency of sol–gel synthesized TiO\textsubscript{2} in photocatalytic degradation of MET

In order to produce highly photocatalytically active nanocrystalline TiO\textsubscript{2} powders by sol–gel route described in details in our previous papers [2, 7], several synthesis parameters, including the type of precursor, alcohol and basic solution, as well as temperature and duration of calcination, have been varied. The first series of the samples were calcined for 7 h, whereas the list of varied synthesis parameters is given in table 1.

Table 1 The list of TiO\textsubscript{2} samples and corresponding sol–gel synthesis parameters [2].
<table>
<thead>
<tr>
<th>Sample name</th>
<th>Precursor</th>
<th>Alcohol</th>
<th>Basic solution</th>
<th>Calcination temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(BE)550</td>
<td>Tetrabutyltitanate (B)</td>
<td>Ethanol (E)</td>
<td></td>
<td>550</td>
</tr>
<tr>
<td>T(CEA)550</td>
<td>Titanium tetrachloride (C)</td>
<td>2-propanol (P)</td>
<td>NH₄OH (A)</td>
<td>550</td>
</tr>
<tr>
<td>T(CPA)550</td>
<td>Titanium tetrachloride (C)</td>
<td>Amyl alcohol (A)</td>
<td>NH₄OH (A)</td>
<td>550</td>
</tr>
<tr>
<td>T(CAA)550</td>
<td>Titanium tetrachloride (C)</td>
<td>Methanol (M)</td>
<td></td>
<td>550</td>
</tr>
<tr>
<td>T(CGA)550</td>
<td>Titanium tetrachloride (C)</td>
<td>Glycerol (G)</td>
<td></td>
<td>550</td>
</tr>
<tr>
<td>T(CAN)400</td>
<td>Titanium tetrachloride (C)</td>
<td>Amyl alcohol (A)</td>
<td>NaOH (N)</td>
<td>400</td>
</tr>
<tr>
<td>T(CAN)550</td>
<td>Titanium tetrachloride (C)</td>
<td>Amyl alcohol (A)</td>
<td>NaOH (N)</td>
<td>550</td>
</tr>
<tr>
<td>T(CAN)650</td>
<td>Titanium tetrachloride (C)</td>
<td>Amyl alcohol (A)</td>
<td>NaOH (N)</td>
<td>650</td>
</tr>
</tbody>
</table>

The XRD patterns of TiO₂ nanopowders (figure 2) have shown the presence of anatase diffraction peaks (JCPDS card 21-1272, space group $I4_1/amd$) with slightly shifted positions [2], indicating a change in lattice parameters in comparison to the bulk values for anatase. Further analysis of the XRD data enabled the assessment of the anatase nanocrystallites size to about 20 nm [2]. Also, the peaks corresponding to the rutile TiO₂ phase (JCPDS card 21-1276, space group $P4_2/mnm$) have been observed in the diffractogram of the sample T(CAN)₆₅₀ and the amount of rutile phase in this sample is estimated to be ~30%. However, as diffraction peaks of brookite TiO₂ phase were not seen in XRD patterns of TiO₂ nanopowders, the Raman spectroscopy method had to be used for the analysis of brookite content.

Typical Raman spectrum of synthesized TiO₂ nanopowder is shown in figure 3a in the range of 50–1000 cm⁻¹. This spectrum, as well as the spectra of all other synthesized nanopowders, is dominated by characteristic anatase Raman modes [2]. Detailed analysis of the most intensive anatase $E_g$ Raman mode has shown nanocrystalline anatase structure with variable stoichiometry and microstrain in all spectra, whereas average anatase crystallite size has been estimated between 17 and 25 nm. Besides, low-intensity Raman modes, ascribed to brookite phase [2], can be also observed in the range from 210 to 380 cm⁻¹ of all spectra (inset of figure 3b). To estimate the amount of brookite phase, the sum of the integrated intensities of Lorentzian peaks, originating from the brookite modes ($I_B$), was compared to the intensity of Lorentzian peak related to the $B_{1g}$ mode of anatase phase ($I_A(B_{1g})$). Although the estimation of brookite modes intensities is unreliable to some extent, due to mode overlapping, a variation in brookite content with synthesis conditions may be roughly estimated from the intensity ratio of brookite to anatase modes, $I_B/I_A(B_{1g})$, shown in figure 3b.

The IR reflectivity spectra of representative TiO₂ nanopowders shown in figure 4 are dominated by the features in the range of 450–1000 cm⁻¹, which can be related to the surface vibration of Ti–O bonds in anatase or mixed anatase/rutile phase (T(CAN)₆₅₀ and Degussa P25). The main spectral features in the region of 1200–4000 cm⁻¹ (shown magnified in the inset of figure 4) appear around 1260 cm⁻¹ (assigned to carbonate or nitrate species at TiO₂ surface [2]), between 1400 and 1800 cm⁻¹ (probably originated from carbonates or hydrogen carbonates groups [10]), and in the ranges of 2800–3000 and 3600–3200 cm⁻¹.
The bands in the range of 2800–3000 cm\(^{-1}\) can be assigned to the symmetric and asymmetric stretching mode of the C–H bond, originating from residues which remain in TiO\(_2\) samples even after calcination [11]. However, the most of attention here is devoted to characterizing O–H groups present at the surface of TiO\(_2\), knowing that in many cases the nature and distribution of these groups are determining factor of catalyst behaviour. So, the vibration band between 3000 and 3150 cm\(^{-1}\) has been associated to the O–H stretching mode of water molecules [12], whereas the one at about 1630 cm\(^{-1}\) has been assigned to O–H bending modes [13]. The bands in frequency range of 3150–3500 cm\(^{-1}\) are usually attributed to H-bounded O–H groups, and those in the 3400–3600 cm\(^{-1}\) region to mixed O–H groups [12]. The bands in the region from 3600 to 3800 cm\(^{-1}\) originate from stretching modes of different types of free hydroxyl groups adsorbed on the crystalline surfaces of titania or from defects located at the surface [13]. It should be noted that IR reflectivity spectra of TiO\(_2\) nanopowders have enabled identification of specified surface groups, but did not allow the relation between the amounts of different kinds of these groups at the surface of TiO\(_2\) nanoparticles to be determined.

![Figure 3](image-url)  
**Figure 3.** Raman spectrum of T(CAA)\(_{550}\) nanopowder with characteristic anatase modes; (b) The intensity ratio of brookite modes, \(\Sigma I_{B}\), to the anatase \(B_{1g}\) mode, \(I_{A}(B_{1g})\) in TiO\(_2\) nanopowders. The inset: Lorentzians of brookite modes in the experimental Raman spectra of sample T(CPA)\(_{550}\) [2].

3200–3800 cm\(^{-1}\). The bands in the range of 2800–3000 cm\(^{-1}\) can be assigned to the symmetric and asymmetric stretching mode of the C–H bond, originating from residues which remain in TiO\(_2\) samples even after calcination [11]. However, the most of attention here is devoted to characterizing O–H groups present at the surface of TiO\(_2\), knowing that in many cases the nature and distribution of these groups are determining factor of catalyst behaviour. So, the vibration band between 3000 and 3150 cm\(^{-1}\) has been associated to the O–H stretching mode of water molecules [12], whereas the one at about 1630 cm\(^{-1}\) has been assigned to O–H bending modes [13]. The bands in frequency range of 3150–3500 cm\(^{-1}\) are usually attributed to H-bounded O–H groups, and those in the 3400–3600 cm\(^{-1}\) region to mixed O–H groups [12]. The bands in the region from 3600 to 3800 cm\(^{-1}\) originate from stretching modes of different types of free hydroxyl groups adsorbed on the crystalline surfaces of titania or from defects located at the surface [13]. It should be noted that IR reflectivity spectra of TiO\(_2\) nanopowders have enabled identification of specified surface groups, but did not allow the relation between the amounts of different kinds of these groups at the surface of TiO\(_2\) nanoparticles to be determined.

![Figure 4](image-url)  
**Figure 4.** IR reflectivity spectra of representa-tive TiO\(_2\) nanopowders. Inset: enlarged part of the IR spectra in the region of 1200–4000 cm\(^{-1}\). Spectra of some powders are upshifted for clarity [2].

More information on the amount of O–H groups in our powders we have obtained from Raman spectra in the C–H and O–H spectral region shown in figure 5. This region is dominated by the broad
feature between 2800 and 3800 cm\(^{-1}\), which can be assigned to O–H stretching vibration of water molecules adsorbed on the surface of the particles and condensed in the pores of TiO\(_2\) nanopowders \[14\], as well as the feature located between 1625 and 1670 cm\(^{-1}\) which can be related to the bending modes of adsorbed water \[10\]. In addition, the peaks in the frequency range of 1200–1500 cm\(^{-1}\) can be associated with carbonate groups \[13\], whereas the peak at 2940 cm\(^{-1}\) can be assigned to the stretching mode characteristic for CH-species \[15\]. However, low intensity peak located at \(\sim 3700\) cm\(^{-1}\) is the most interesting one in this analysis. Namely, this feature, assigned to the O–H stretching mode of isolated (free) hydroxyls \[10\], can be related to the ability of the anatase samples to form the surface O–H groups, with the important influence on their catalytic activity \[16\]. According to several authors, the hydroxyl groups with vibration frequency at \(\sim 3700\) cm\(^{-1}\) are the most photocatalytically active among all hydroxyl groups at the surface of TiO\(_2\) nanoparticles \[13\].

The influence of the different synthesis parameters on the photocatalytic efficiency of TiO\(_2\) nanopowders in degradation of MET under UVA light irradiation are presented in figure 6, together with the results obtained using commercially available Degussa P25 under the same conditions. From figure 6a, which illustrates the influence of the type of precursor on TiO\(_2\) nanopowders photocatalytic activity, it can be seen that the activity of TiO\(_2\) nanopowders synthesized with titanium tetrachloride as precursor is much higher, but still somewhat lower than of Degussa P25. The influence of the type of alcoh gel on photocatalytic activity of TiO\(_2\) nanopowders (figure 6b) was examined by using different alcohols during the synthesis. As can be seen, the highest photocatalytic activity showed the catalysts obtained using methanol and amyl alcohol. The figure 6c shows the influence of calcination temperature on the photocatalytic activity of TiO\(_2\) nanopowders on MET photodegradation. It can be seen that the TiO\(_2\) nanopowders calcined at \(\geq 550\) °C showed the highest photocatalytic activity, even slightly higher than Degussa P25.

![Figure 6](image_url)

**Figure 6.** Kinetics of photocatalytic degradation of MET \((c_0 = 0.05\) mM\) in the presence of sol–gel synthesized TiO\(_2\) nanopowders and Degussa P25 \((1.0\) mg mL\(^{-1}\)). The influence of different synthesis parameters: (a) precursor, (b) alcohol and (c) calcination temperature \[2\].

Structural analysis of synthesized nanopowders by XRD and Raman spectroscopy, briefly presented here, has shown that different mixtures of TiO\(_2\) crystal modifications (anatase, rutile, and brookite) were obtained with proper choice of synthesis parameters. It has been noticed that the content of brookite decreased photocatalytic activity in synthesized nanopowders with other properties comparable, whereas the amount of rutile did not have critical impact on the photocatalytic activity. So, it could be concluded that structural properties of nanopowders had some impact on their photocatalytic activity, but not decisive. On the other side, the results obtained from BET (Brunauer-Emmett-Teller) analysis for the specific surface area, and especially pore size distribution \[2\], have led to unambiguous conclusions that larger surface area and greater number of pores with dimensions in mesoporous region \((> 2\) nm\), produced higher photocatalytic degradation of MET, as a material with relatively large molecules (with molecular size of 0.610 nm × 1.347 nm \[7\]). Also, isolated hydroxyl groups on the
surface of TiO$_2$, which can trap holes to generate the photocatalytically important active species, i.e. *OH radicals [17], have appeared as one of decisive factors in high photocatalytic efficiency of TiO$_2$ in degradation of MET. Namely, as can be seen from figure 5, the Raman mode at ~3700 cm$^{-1}$, originating from isolated O–H groups, appears in the spectra of all samples with relatively high photocatalytic activity (including Degussa P25), and it is hardly detected in T(CAN)$_{400}$ with relatively poor activity.

In the second series of anatase nanopowders prepared by sol–gel method, the structural and morphological properties have been modified by varying the duration of calcination at 550 °C from 1 to 7 h, with the other synthesis parameters same as for the CAN samples from the first series. The XRD analysis has shown that extending of calcination time caused slight growth of crystallites in synthesized samples (from 13 to 17.5 nm), with the other structural properties similar [7]. Raman scattering data confirmed the anatase as dominant TiO$_2$ phase, with the presence of small amount of brookite in some samples [7]. The nonstoichiometry, revealed from the additional broadening and blueshift of the most intensive Raman $E_g$ mode, could not be clearly correlated to the calcination time [7]. The analysis of nitrogen sorption data has shown that the specific surface area was greater in the samples with shorter calcination time (up to 4 h), whereas the greatest mean pore diameter was registered in the sample calcined for 4 h (figure 7a). Additionally, the corrugated pore structure model was employed to evaluate tortuosity factor which provides the information on the connectivity among the pores, essential to describe transport dynamics in porous media [18]. This model has shown that tortuosity factor increased with increasing calcination time up to 4 h, and then gradually decreased for a longer time of calcination (figure 7b). The study of photocatalytic efficiency in degradation of MET has demonstrated that samples calcined for 4 and 5 hours have displayed higher photocatalytic performance than Degussa P25, whereas the sample calcined for 3 hours has shown comparable activity, as can be seen from the dependence of reaction rate constant on calcination time shown in figure 7c. Since the analysis of XRD and Raman spectroscopy data have shown that there is no great variation in structure and phase composition of synthesized powders, the main reason for different efficiency in photocatalytic degradation of MET should have been seeking in the structural properties of these powders. However, the powder calcined for 1 h, with the greatest specific surface area $S_{BET}=182$ g cm$^{-3}$, has the poorest photocatalytic efficiency of all examined samples. At the same time, some nanopowders with smaller $S_{BET}$ value have relatively good photocatalytic activity [7].

On the other hand, maximal photocatalytic efficiency was reached in the sample calcined for 4 h, in which mean pore diameter has the greatest value, as well as tortuosity factor. Moreover, calculated reaction rate constant in degradation of MET (figure 7c) behaves similarly as mean pore diameter with calcination time varied. The same tendency is especially expressed in dependence of tortuosity factor on calcination time (figure 7). These relationships confirm the crucial role of the pore size distribution and tortuosity factor as a measure of the pore structure complexity in efficient photocatalytic degradation of relatively large pollutant molecules such as MET.

3. Surface modification of sol–gel synthesized TiO$_2$ nanoparticles induced by La-doping

The influence of La-doping in the range of 0.5–6.0 mol% on structural, morphological, surface and electronic properties of TiO$_2$ photocatalysts, prepared by sol–gel method, have been extensively characterized in order to correlate the change in these properties with TiO$_2$ photocatalytic efficiency in degradation of MET in aqueous solution under UVA light irradiation. The XRPD and Raman
measurements have revealed the anatase phase as dominant in all synthesized nanopowders, with crystallite size decreasing from ~15 nm in pure TiO$_2$ to ~12 nm in La-doped samples [8]. The analysis of nitrogen sorption data has shown that all samples are fully mesoporous, with a mean pore diameters in the range of ~6–8 nm, as well as the increase of specific surface area and pore structure complexity with doping [8]. The SE has apparently shown that direct bandgap energy has been gradually increased with the increase of La content (figure 8). The AFM, STM, and STS techniques have been used successfully to evaluate the surface morphology and electronic properties of La-doped nanopowders. It can be seen from nc-AFM images of pure and 6 mol% La-doped TiO$_2$ samples (Figs. 9a and 9b, respectively) that investigated nanopowders consist of very small nanocrystals (up to 20 nm) and greater agglomerated particles. In the close-up image of the sample with 6 mol% La (figure 9c) one could observe a granular structure (up to 2 nm) covering the surface of some nanoparticles. Since TiO$_2$ nanoparticles with both smooth and rough surface in that sample have also been distinguished by the STM, STS measurements have been used to obtain information on surface bandgap in the nanoparticles with different surface morphologies. The figure 10(a) shows a typical d$I$/d$V$ versus $V$ characteristic of isolated TiO$_2$ particles with smooth surface and its STM image in the inset. From presented STS data, the surface bandgap of those particles has been estimated as ~3.2 eV, a value close to bandgap of anatase phase. However, in the same sample, for isolated TiO$_2$ particles covered with rough granular structure (figure 10(b)), the higher value of surface bandgap (~4 eV) has been found, implied that granular structure was most probably consisted of La$_2$O$_3$. These results have supported the findings of the SE that gradual increase of direct bandgap energy with La-doping could be attributed to the surface modification of TiO$_2$ nanoparticles due to the presence of La$_2$O$_3$.

**Figure 8.** The plot of $(\alpha E)^2$ versus $E$ for direct bandgap transition in pure and La-doped TiO$_2$ nanopowders samples with characteristic tangent lines. Inset: the dependence of estimated direct bandgap energy on mol% of La [8].

**Figure 9.** The nc-AFM images of TiO$_2$ samples: (a) pure, (b) doped with 6 mol% La, and (c) close-up image of the second one [8].

**Figure 10.** Differential $dI/dV$ versus voltage, $V$, characteristics of isolated TiO$_2$ nanoparticles of the sample doped with 6 mol% La, with (a) smooth and (b) rough surface obtained by STS, together with corresponding STM images in the insets [8].
The study of photocatalytic activity has revealed that all doped samples showed increased photocatalytic activity compared to pure TiO$_2$, among which the 0.65 mol% La-doped sample appeared to be the most efficient (figure 11). The improvement in photocatalytic properties of La-doped samples can be ascribed to the formation of La$_2$O$_3$ at the grain boundaries of anatase nanoparticles. This effect inhibits the growth of crystal grains, decreasing of anatase crystallite size and produce more complex pore structure [19], which is confirmed by the results of XRPD, Raman and physisorption measurements. It should be also noted that the presence of isolated hydroxyl groups on the surface of TiO$_2$ nanoparticles, which could represent decisive factor for high photocatalytic activity in degradation of MET [2], has been registered only in the nanopowders with low level of La-doping - 0.65 and 1 mol% [8]. This implies that reduction of photocatalytic activity of TiO$_2$ nanopowders with further increase of La-doping amount may be related to the blocking of the active centres due to the accumulation of excess La$_2$O$_3$ on the surface of anatase grains, registered by both AFM and STM measurements.

4. Brookite type TiO$_2$ nanopowders prepared using hydrothermal route in photocatalytic degradation of alprazolam

Photocatalytic degradation of alprazolam has been investigated in aqueous solutions containing nanocrystalline brookite-type powders, synthesized by combination of sol–gel and hydrothermal method, with titanium tetrachloride (TiCl$_4$) as a precursor, and hydrothermal temperature and reaction time varied in the range of 120–200 °C and 12–48 h, respectively. The XRPD patterns (figure 12, left panel) have shown that pure brookite phase (JCPDS card 29-1360, space group $Pbca$) has been obtained.
only in the sample $B_{200/24}$, synthesized at 200 °C, after 24 h of hydrothermal process. In all other samples anatase phase also appears, whereas rutile and sodium titanate phases have been noticed in the samples synthesized at lower temperatures. The presence of different titania phases has also been confirmed by Raman spectra shown in figure 13.

The SEM micrographs (figure 12, right) have shown spindle-like particles in brookite-rich samples synthesized at 200 °C, whereas BET measurements have detected mesoporous structure in these samples [9]. The dependence of $(\alpha E)^{1/2}$ plots on the photon energy for an indirect transition, as well as the $(\alpha E)^2$ plots for a direct transition, obtained from SE data, are shown in Figs. 14(a) and 14(b), respectively. The energies of indirect and direct transition in pure brookite sample ($B_{200/24}$), estimated as ~ 2.5 eV and ~3.85 eV, respectively, seemed to have higher values compared to the other samples synthesized at 200 °C ($B_{200/12}$ and $B_{200/48}$), consisted from anatase and brookite.

![Figure 14](image_url)  
**Figure 14.** The plot of (a) $(\alpha E)^{1/2}$ and (b) $(\alpha E)^2$ versus $E$ for indirect and direct bandgap transition in synthesized powders, respectively, with characteristic tangent lines for pure brookite sample [9].

![Figure 15](image_url)  
**Figure 15.** Photocatalytic efficiency of synthesized brookite type powders and Degussa P25 in the removal of alprazolam ($c_0 = 0.03$ mM) [9].

The kinetics curve of alprazolam removal using synthesized brookite type nanopowders have revealed that the sample consisted of pure brookite has shown the highest efficiency in the photodegradation of alprazolam, removing more than 98% of alprazolam in the first 30 minutes of photocatalytic reaction. The other brookite-rich powders, synthesized at 200 °C, have also shown high photocatalytic efficiency, whereas the powders consisted dominantly of sodium-titanate, produced at lower temperatures (120 and 160 °C), have been almost photocatalytically inactive in degradation of alprazolam. Improved photocatalytic efficiency of the pure brookite sample in photodegradation of alprazolam has been mainly ascribed to increased amount of brookite phase in the hydrothermally synthesized TiO$_2$ samples, rather than brookite crystallite size and specific surface area of nanopowders. Such improvement may be also related to higher energy of direct and indirect transitions in pure brookite sample, as well as a slight increase of the most frequent pore diameter with the increase of brookite content in brookite-rich samples.

5. Conclusion
This study has shown that different mixtures of TiO$_2$ crystal modifications (anatase, rutile, and brookite) could be obtained with proper choice of synthesis methods and parameters. It has been also demonstrated that any changes in sol–gel and/or hydrothermal synthesis conditions, however small, could have significant effects on the synthesised TiO$_2$ nanoparticles and consequently on their photocatalytic properties. According to this, careful control of the overall synthesis conditions and the intentional variation of some individual parameters allowed us to synthesize pure and La-doped anatase nanopowders suitable for photocatalytic degradation of MET, as well as brookite-type TiO$_2$ nanopowders for degradation of alprazolam, with photocatalytic performance comparable or even better
than commercially available Degussa P25 TiO₂ nanopowder. At the same time it has been shown that decisive factors for enhanced photocatalytic efficiency in degradation of different pollutants, such as MET and alprazolam, did not have to be the same. For instance, the sample consisted of pure brookite has shown the highest efficiency in the photodegradation of alprazolam, whereas a higher content of brookite (although its highly disordered phase) was not favourable for photocatalytic degradation of MET. The high efficiency of TiO₂ catalysts in photodegradation of MET, as a material with relatively large molecules, has been more correlated with large specific surface area of nanopowders and great number of well-connected pores with dimensions in mesoporous region (> 2 nm). Also, the presence of isolated hydroxyl groups on the surface of TiO₂ which can trap holes to generate •OH radicals, as the photocatalytically important active species, has appeared as one of crucial factors in high photocatalytic efficiency of TiO₂ in degradation of MET. These findings not only have pointed to different degradation mechanisms of the investigated pharmaceutical compounds in the presence of different catalysts, but also have launched further research to deepen understanding of those mechanisms.

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References