Mechanochemical and microwave treatment of precipitated zirconium dioxide and study of its physical–chemical, thermal and photocatalytic properties

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Abstract
The effects of the microwave treatment (MWT) and mechanochemical treatment (MChT) on the structure and physicochemical properties of precipitated zirconium oxide were investigated. The obtained materials were characterized using the N2 adsorption/desorption, thermogravimetry (TG, DTG, DTA), XRD and UV–Vis/DRS methods. Photocatalytic properties of the samples were also studied as regards the rhodamine B (RhB) degradation in the aqueous solution. The results show that the microwave and MChT, differing in mill rotation speed, temperature or treatment media, causes significant changes in the porous structure of the obtained samples. In most samples, the specific surface area increase was observed. The DTA and XRD results showed the formation of crystalline structure during MWT. As follows from the investigations, each way of modification results in the shift of the absorption edge toward higher wavelength values and causes photocatalytic degradation of RhB under UV irradiation and makes the obtained materials effective photocatalysts in the visible region.

Keywords Zirconium oxide · Microwave treatment · Mechanochemical treatment · Porous structure · Thermal analysis · Photocatalysis

Introduction
Zirconium dioxide is a versatile material. As this oxide can be obtained in a highly dispersed state (as non-porous and porous powders or porous xerogels), it is widely applied as the catalysts, the adsorbent or the support for catalysts [1–4]. Its use as a photocatalyst is confined by a large band gap: 3.5–5.0 eV depending on preparation methods and calcination conditions [5–8]. Therefore, ZrO2 exhibits photocatalytic activity only under UV-irradiation [8–10]. All these applications require certain crystal structure and electronic characteristics as well as developed specific surface area and porous structure of ZrO2. The disadvantages of zirconium dioxide obtained by conventional methods (such as precipitation, sol–gel) are a significant content of micropores and an underdeveloped mesoporous structure. Modification of precipitated oxides allows to control porous structure parameters. The hydrothermal method is the most effective for preparation of crystalline ZrO2 with a developed mesoporous structure. The effect of classical hydrothermal treatment (in autoclaves) on zirconium dioxide structure was earlier studied by Chertov and co-workers as well as Shar- ygin and co-workers. These results are summarized in the reviews [11, 12].

A similar effect but in a shorter time can be achieved using the hydrothermal treatment with microwave heating (microwave treatment, MWT) [13–15]. As well hydrother- mal conditions are satisfied during the mechanochemical treatment (MChT) in water [16, 17]. Additional possibilities for adjusting the parameters of the porous structure are provided by modification in the wet gel stage before drying.
This was exemplarily confirmed using oxides and phosphates [19–22]. Moreover, the efficiency of MWT and MChT application for regulation of physical–chemical properties of other semiconductor oxides was demonstrated in the studies [20, 23–26]. The analysis of the literature data shows that oxides with different characteristics and improved photocatalytic and adsorption properties can be obtained by varying the treatment conditions.

Taking into account the results obtained in those papers, combination of the two approaches (MWT and MChT as well as their use in the wet gel stage) is encouraging for precipitated ZrO₂. Moreover, the effect of MWT and MChT on the porous structure of zirconium dioxide has not been reported before.

The aim of this paper was to study the effect of microwave (MWT) and mechanochemical treatment (MChT) on the porous, crystalline and electronic structure of the precipitated ZrO₂. The changes in the photocatalytic activity of the obtained samples as a result of those in the physicochemical characteristics were also examined.

Experimental

**Synthesis of ZrO₂**

The gelatinous precipitate (coagel) of ZrO₂ was prepared by applying the common procedure: the gradual addition (1 mL min⁻¹) of 10% aqueous NH₄OH solution to the 0.2 M solution of ZrOCl₂·8H₂O with vigorous stirring. At the end of precipitation, the pH value was 5. The coagel was ripened in the mother liquor for 12 h, then it was washed with distilled water until a negative reaction toward Cl⁻ ions took place. Finally, coagel was compacted on the filter to a moisture content of about 85% w/w. It was granulated by extrusion and dried at 20 °C for 30 h for preparation of xerogel. Part of the wet gel (coagel) was subjected to MWT and MChT on the porous structure of zirconium dioxide has not been reported before.

The aim of this paper was to study the effect of microwave (MWT) and mechanochemical treatment (MChT) on the porous, crystalline and electronic structure of the precipitated ZrO₂. The changes in the photocatalytic activity of the obtained samples as a result of those in the physicochemical characteristics were also examined.

**Procedures of ZrO₂ modification**

**Microwave treatment (MWT)**

The modification processes were conducted using the NANO 2000 high-pressure reactor (Plazmatronika, Poland, 650 W). The temperature and time of treatment duration were 150 and 190 °C and 0.5 h, respectively. The pressure was 1 and 1.5 MPa. About 35 g of the initial wet coagel was placed in a quartz tube and inserted in the reactor with 20 mL of water. After modification, the material was dried at 20 °C for 24 h. As a result, the materials designated: MWT_{gel-150 °C} and MWT_{gel-190 °C} were obtained.

**Mechanochemical treatment (MChT)**

The MChT was conducted using a planetary ball mill Pulverisette 7 Premium Line (Fritsch, Germany). Milling was performed in both air atmosphere and water. The container and milling balls were made of Si₃N₄. 25 balls of 10 mm diameter (total balls mass was 40 g) were used. The mass of loaded wet gel and dried xerogel was 42 g and 5 g, respectively. 35 mL of water was added into the vessel when the xerogel was subjected to MChT in water. The MChT was performed at the mill rotation speeds: 200, 300, 500, 600 and 800 rpm for 0.5 h. After modification, the material was dried at 20 °C for 24 h. The type of modification, type of starting material and modification conditions are given in the sample designations, e.g., MChT_{gel-600 rpm} (mechanochemical treatment of coagel at 600 rpm), MChT_{xerogels/water-300 rpm} (mechanochemical treatment of xerogels with the water addition at 300 rpm), etc.

In addition, the initial ZrO₂ xerogel was subjected to the thermal modification at 400 °C for 5 h (the sample designated ZrO₂-TT-400 °C). This temperature was selected from the DTA-TG data.

**Characterization methods**

**Nitrogen adsorption/desorption**

The nitrogen isotherms of adsorption–desorption were obtained using an automatic gas adsorption analyzer ASAP 2405 N (Micromeritics Instrument Corp., USA) after outgassing of the samples at 150 °C for 2 h. The specific surface area S_{BET}, mesopores volume (V_{me}) and micropores volume (V_{mi}) were calculated from these isotherms using the BET, BJH and t-plot methods, respectively [20]. The sorption pore volume V_s was determined at a relative pressure p/p⁰ close to 1. The total pore volume V_p was determined by means of impregnation of the dried samples (drying at 150 °C for 2 h) with liquid water. This is so-called the incipient wetness method [27]. The sorption pore volume V_s includes the volume of micro- V_{mi} and mesopores V_{me}, which can be filled during sorption from the vapour phase. Macropores, on the other hand, are filled applying liquid impregnation. Therefore, the volume of macro pores V_{ma} is calculated as the difference V_p – V_s [28–30]. The curves of pore size distribution (PSD) were plotted using the desorption branches of isotherms [28]. The pore radius R_p was determined from the PSD curves.

**XRD**

The initial ZrO₂ and the materials obtained after modification were studied by the X-ray powder diffraction (XRD, Empyrean, USA) using the Philips PW 1830 diffractometer with CuKα radiation. The X-ray patterns were scanned in the 2Θ range.
range of 10°–60° with a step 0.02°. The crystallite size for ZrO₂ was calculated according to the Scherrer formula using the reflex at 30.2°.

**DTA-TG**

The curves of DTA and TG were recorded using the Derivatograph-C apparatus (F.Paulik, J.Paulik, L.Erdey) in the temperature range of 20–800 °C at a heating rate of 10°/min. The initial sample mass was 30 or 200 mg.

**UV–Vis diffuse reflectance spectroscopy**

The diffuse reflectance UV–Vis/DRS spectra of the samples were registered using the UV–Vis/DRS Lambda 35 UV–Vis spectrometer (Perkin-Elmer Instruments). MgO was used as reference sample. The spectra were recorded in the range 200 – 600 nm. The absorption edge λ of the obtained samples was determined using spectra plotted in the Kubelka–Munk equation coordination. The value of the band gap E₉ was calculated from the Planck equation:

\[ E_g = \frac{1239.5}{\lambda} \]  

(1)

**Photocatalytic test**

Photocatalytic activity of the selected samples was tested in relation to the aqueous solution of rhodamine B (RhB, \( C_0 = 0.5 \cdot 10^{-5} \) mol L⁻¹) in the range of ultraviolet (UV) and visible (Vis) radiation. High-intensity discharge Na-lamp GE Lucalox (Hungary, 70 W), which irradiates solely in the visible region, was used as the Vis light source while photodegradation using the UV light was conducted in a quartz reactor using the Hg lamp (254 nm, 30 W). The ratio of catalyst (mg) to the solution (mL) was 1:1. The solution was mixed with the weighed sample using a magnetic stirrer without light access for 60 min to determine the balance of adsorption / desorption of the dye on the photocatalyst surface. During the specific time about 3 mL of the reaction mixture was collected, centrifuged (10 min, 8000 rpm) and analyzed using the spectrophotometer (Lambda 35, Perkin-Elmer Instruments) at \( \lambda = 554 \) nm. The photodegradation constants \( K_{d}^{UV} \) and \( K_{d}^{Vis} \) were calculated on the basis of the concentration changes of the dye solution after the adsorption/ desorption equilibrium establishment.

**Results and discussion**

**Crystal structure**

It is well known that ZrO₂ exists in three polymorphs at the atmospheric pressure [5]: the monoclinic, the tetragonal, and the cubic fluorite, denoted as m-, t-, and c-ZrO₂, respectively. However, zirconium dioxide precipitated from the aqueous solution is often X-ray amorphous. Figure 1 presents the patterns of the initial coagel iniZrO₂ as well as the materials after thermal (ZrO₂-TT-400°C) and microwave (MWT<sub>gel-150 °C</sub> and MWT<sub>gel-190 °C</sub>) treatment. As the initial material (iniZrO₂), the samples after MChT were X-ray amorphous (these diffractograms were not shown). This experimental fact is in full agreement with the general tendencies of changes in the crystal structure during the mechanochemical treatment. This concerns the disordering effect of MChT on the structure of oxides in general [20–23, 25, 26] and zirconium dioxide in particular [31]. Therefore, it is unlikely that crystallization of ZrO₂ can occur due to the milling of amorphous form.

On the contrary, after the thermal and microwave treatment the appearance of peaks for crystalline ZrO₂ was observed. That indicates the formation of the zirconium crystalline structure. The XRD pattern for a sample treated at 400 °C (ZrO₂-TT-400°C) indicates that this material has a practically pure tetragonal phase as evidenced by the peaks located at 2θ = 30.2° (the most intense) and 2θ = 35.2° and 50.6° (JCPDS No. 50–1089). Thermal treatment promotes the crystallization process and the growth of ZrO₂ crystallites only at 400 °C. For ZrO₂-TT-400°C, the crystallite size was 15 nm. The patterns recorded for the samples after MWT indicate the presence of both tetragonal (2θ = 30.2°, 35.2° and 50.6°) and monoclinic (2θ = 24.4° and 28.2°) phases but with a predominance of t-ZrO₂ phase. The comparison of the MWT<sub>gel-150 °C</sub> and MWT<sub>gel-190 °C</sub> patterns indicates that the use of a higher MWT temperature results in the development of both monoclinic and tetragonal crystalline phases (Fig. 1). The crystallite sizes for...
these materials are 5 and 5.5 nm, respectively. Therefore, MWT allows to prepare tetragonal ZrO$_2$ at a lower temperature compared to the thermal treatment. As a result, more dispersed crystalline phase is formed than after the thermal treatment.

**Porous structure**

The examples of nitrogen adsorption/desorption isotherms for the tested samples are shown in Fig. 2. As follows from the analysis of the adsorption isotherms course, they are of I and IV types according to the IUPAC classification [29]. The course of the curves for iniZrO$_2$ (Fig. 2) indicates that they are type I isotherms without the hysteresis loop. These isotherms are characteristic of the monolayer adsorption on the microporous materials [30]. Nonetheless the iniZrO$_2$ sample contains mesopores of the minimal average pore radius, that is $R_p = 1.3$ nm (Table 1). The course of the isotherms for the materials after modification in the presence of water (Fig. 3) indicates that both the mechanochemical and microwave treatment causes the development of a porous structure. The isotherms are located higher and the hysteresis loops are gradually shifted higher relative to the $p/p_0$ axis which indicates the surface and mesoporosity development of the obtained materials. This is the most evident in the case of materials obtained using the microwave energy (MWT$_{gel-150 \, ^\circ C}$ and MWT$_{gel-190 \, ^\circ C}$). The course of the curves for these materials indicates that these are type IV isotherms with developed hysteresis loops of type H2 which are characteristic of mesoporous materials, in the pores of which the phenomenon of capillary condensation is observed. According to Sing et al. [32], the course of these hysteresis shape indicates presence of pores with narrow mouths (ink-bottle pores), relatively uniform channel-like pores, pore network (connectivity) effects. At the same time, MWT leads to removal of micropores by turning them into mesopores (Fig. 2; Table 1). The size of the latter increases to 3.7–4.7 nm. This is caused by mass transfer processes and crystallization of amorphous phase [11]. The latter is accompanied by formation of a denser phase and corresponding generation of additional porosity according to the Pilling–Bedworth ratio [33, 34]. As can be seen using the microwave treatment of coagel (Fig. 2, MWT$_{gel-150 \, ^\circ C}$ and MWT$_{gel-190 \, ^\circ C}$) resulted in a greater increase in mesoporosity than the use of mechanochemical treatment (Fig. 2, MChT$_{gel-300 \, rpm}$). However, the changes in the specific surface area are more significant after MChT of gel (Table 1).

Figure 3 presents the N$_2$ adsorption isotherms for the samples obtained as a result of mechanochemical treatment in the form of dried xerogel (in water or air) using

![Fig. 2 The low-temperature adsorption/desorption isotherms of nitrogen obtained for the exemplary samples](image-url)

**Table 1 The parameters of the porous structure for some samples**

| Sample                  | $S_{BET}$/m$^2$ g$^{-1}$ | $V_0$/cm$^3$ g$^{-1}$ | $V$/cm$^3$ g$^{-1}$ | $V_m$/cm$^3$ g$^{-1}$ | $V_m$/cm$^3$ g$^{-1}$ | $V_{ma}$/cm$^3$ g$^{-1}$ | $R_p$/nm |
|-------------------------|--------------------------|-----------------------|---------------------|-----------------------|------------------------|------------------------|---------|
| iniZrO$_2$              | 130                      | 0.07                  | 0.07                | 0.04                  | 0.03                   | 0                      | 1.3     |
| MChT$_{gel-200 \, rpm}$ | 199                      | 0.19                  | 0.10                | 0.06                  | 0.04                   | 0.09                   | 1.35    |
| MChT$_{gel-300 \, rpm}$ | 264                      | 0.18                  | 0.14                | 0.10                  | 0.04                   | 0.04                   | 1.35    |
| MChT$_{gel-500 \, rpm}$ | 251                      | 0.20                  | 0.16                | 0.12                  | 0.04                   | 0.04                   | 1.45    |
| MChT$_{gel-600 \, rpm}$ | 255                      | 0.24                  | 0.15                | 0.12                  | 0.03                   | 0.09                   | 1.6     |
| MChT$_{gel-800 \, rpm}$ | 277                      | 0.27                  | 0.15                | 0.10                  | 0.05                   | 0.12                   | 1.55    |
| MChT$_{xerogel \, air-200 \, rpm}$ | 243             | 0.15                  | 0.14                | 0.11                  | 0.03                   | 0.01                   | 1.35    |
| MChT$_{xerogel \, air-300 \, rpm}$ | 75              | 0.07                  | 0.07                | 0.06                  | 0.01                   | 0                      | 1.3; 3.35 |
| MChT$_{xerogel \, water-200 \, rpm}$ | 97            | 0.26                  | 0.06                | 0.04                  | 0.02                   | 0.2                    | 1.35    |
| MChT$_{xerogel \, water-300 \, rpm}$ | 86           | 0.23                  | 0.07                | 0.06                  | 0.01                   | 0.16                   | 1.35;9.45 |
| MChT$_{xerogel \, water-800 \, rpm}$ | 88          | 0.17                  | 0.08                | 0.06                  | 0.02                   | 0.09                   | 1.4; 7.25 |
| MWT$_{gel-150 \, ^\circ C}$ | 164             | 0.23                  | 0.17                | 0.17                  | 0                      | 0.06                   | 1.85    |
| MWT$_{gel-190 \, ^\circ C}$ | 163             | 0.31                  | 0.22                | 0.22                  | 0                      | 0.09                   | 2.35    |
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The isotherms for the samples milled at 300 rpm have a poorly pronounced hysteresis loop of type H4. On this basis, it can be concluded that the modified materials have pores of different shapes: narrow slit-like pores, particles with internal voids of irregular shape and broad size distribution, hollow spaces between the particle walls [32].

In the case of mechanochemical treatment in air, the intensive development of porous structure (Fig. 3) occurs using a slower mill rotation speed (MChTxerogel/air-200 rpm, Fig. 3; Table 1). An increase in the mill rotation speed (MChTxerogel/air-300 rpm) results in an approximately three-fold reduction of $S_{BET}$ compared to MChTxerogel/air-200 rpm. An inverse relationship for the mechanically treated samples with the addition of water is observed. In this case, the $S_{BET}$ of this material decreases as the mill rotation speed increases (Table 1). The dependences of the specific surface area and the total pore volume on the conditions of MWT and MChT (temperature and rotation speed) are shown in Fig. 4a, b.

As can be seen after MChT of ZrO$_2$, mostly in the form of wet gel, the specific surface area ($S_{BET}$) of the obtained materials increased (MChTgel series) about twice as compared to the surface of the initial material (iniZrO$_2$, $S_{BET} = 130$ m$^2$ g$^{-1}$, Table 1). Such tendency along with the increase in mill rotation speed is observed for the coagel based materials (Fig. 4a; Table 1). The highest $S_{BET}$ value for the MChTgel-800 rpm sample was observed (Table 1, $S_{BET} = 277$ m$^2$ g$^{-1}$, Fig. 4a). For the discussed materials (MChTgel series), during the increase in mill rotation speed, the pore volume ($V_\Sigma$, $V_s$, $V_{me}$) and $R_p$ (Table 1, Fig. 4b) increase. It should be noted that similar results were earlier obtained for silica, tin dioxide and zirconium phosphate after their MChT [19–21]. It is well known that the specific surface area and pore volume depend on the globules size and their packing density in the skeleton of globular porous solids [29]. Obviously, repackaging of globules occurs only during MChT in the presence of water. An increase in the specific surface area after MWT is due to formation of a more dispersed crystalline phase in the amorphous matrix which is characteristic for hydrothermal conditions [11]. On the contrary, mass transfer processes cause its decrease. Therefore, a resulting effect of increase in the specific surface area at MWT is not as significant as at MChT of wet gels. In the latter case, the processes of crystallization and mass transfer do not play a significant role but those of grinding and repackaging
globules in the gel skeleton are of remarkable importance. As a result, a more accessible for nitrogen molecules structure, containing meso- and macropores, is formed in the drying stage. The specific surface area obviously increases after MChT in air at the minimal intensity (200 rpm) for the same reason. Reduction in the specific surface area and pore volume values, observed at greater intensity, is due to the destruction of xerogel rigid structure affected by the mechanical forces.

The pore volume distribution curves by their average radius (dV/dR, Fig. 5a–d) confirm the results presented in Table 1. Most of the obtained materials have a monomodal character. However, the bimodal pore structure was observed as the mill rotation speed increased (Table 1, Fig. 5b). In the case of dV/dR curves recorded for the mechanochemically treated samples (both in air and with the addition of water) at 200 rpm, one can observe clearly formed maxima indicating the presence of narrow mesopores ($R_p \sim 1.3$ nm, Fig. 5a). Comparing Figs. 5a and b formation of pores of differentiated sizes (Fig. 5b) for the xerogel materials can be observed as the mill rotation speed increases.

Figure 5c, d presents the pore volume distribution curves relative to their average radii for the samples modified in the form of wet gel. The course of the analyzed curves indicates that the increase in the mill rotation speed (Fig. 5c) causes an increase in the pore volume, the size of which does not change ($R_p \sim 1.4$ nm). Moreover, one

![Fig. 5](image)

Fig. 5 The pore volume distribution functions (dV/dR) regarding their radius for some samples (a–d)
can see that the fraction of pores with a radius greater than 2 nm increases after MChT of gel. The increase in temperature used during the microwave treatment (Fig. 5d) resulted in both the volume ($V_\Sigma$, $V_s$) and the average pore radius increase (Table 1; Fig. 4b). It should also be noted that modification in the presence of water (MWT and MChT) leads to formation of macropores, as indicated by the excess of $V_\Sigma$ over $V_s$ (Table 1). This is due to the fact that macropores are filled by means of only liquid impregnation as mentioned above.

**DTA-TG measurements**

The results of thermogravimetric analysis complement well and confirm the investigations of the crystalline and porous structure. The curves of DTA-TG-DTG for some selected samples are presented in Fig. 6a–c. Thus, the curves, typical of amorphous zirconium dioxide and discussed in the literature [35–37], were obtained for the initial sample and that milled at 600 rpm in the form of wet gel (Fig. 6a, b). The sharp exo-effects on the DTA curve at 436 and 427 °C, respectively, indicate crystallization of amorphous ZrO$_2$ and confirm the XRD results. The very similar curves recorded for the other milled samples are also X-amorphous. The DTA curve registered for the crystalline sample MWT$_{gel-190}$ °C contains only poorly diffused exo-effects with the maxima at 397 and 473 °C (Fig. 6c). These effects can be attributed to the crystallization amorphous phase residues and transformation of formed m-ZrO$_2$ into t-ZrO$_2$. It should be noted that a much larger sample was used in the measurement compared to the first two samples: 200 mg versus 30 mg.

Endo-effects in the temperature range up to 200 °C, which are accompanied by the mass loss ($\Delta m_{20-200}$), are associated with removal of physically adsorbed water from pores. Therefore, the $\Delta m_{20-200}$ value is directly related to the pore size: the smaller the pore size, the greater the mass loss

![Fig. 6](image) The curves of DTA, TG and DTG for the initial sample–mass 30 mg a, the sample milled as gel at 600 rpm MChT$_{gel-600}$ rpm–mass 30 mg b, the sample after MWT gel at 190 °C–mass 200 mg c.
Δm_{20–200}. This can be seen comparing the data in Table 1 (column 8, \(R_p\)) and Table 2 (column 4, \(Δm_{20–200}\)). Two endoeffects are observed for the initial and milled samples (Table 2, column 2, \(t_{endo}\)): low and high temperature. Obviously they correspond to removal of water from the meso- and micropores, respectively. There is a low-temperature endoeffect only for the sample after MWT since it does not contain micropores.

The second stage of mass loss in the temperature range 200–500 °C (\(Δm_{200–500}\)) is attributed to the dehydroxylation processes [33, 34]. As can be seen from column 5 of Table 2, the value of \(Δm_{200–500}\) is within 6.4–7.2% w/w, almost the same for all studied samples.

### Electronic structure

Figure 7 presents the UV–Vis/DRS spectra recorded for the initial and some modified samples. For the iniZrO\(_2\) sample, the absorption edge is at \(λ = 268\) nm. As follows, the value of band gap energy was \(E_g = 4.63\) eV (Table 3) which is consistent with the literature data [6, 7]. Thus, this material shows strong absorption in the UV region (Table 3, Fig. 7). All kinds of modification result in the absorption edge shift toward a longer wavelength—the bathochromic shift \(∆λ\). As a result, narrowing the band gap \(E_g\) takes place (Table 3). The mill rotation speed has a significant effect on the value of \(E_g\). It can be concluded that the increase in mill rotation speed resulted in reduction in band gap energy by 0.79 eV if compare the \(E_g\) values for the MChT xerogel/water-300 rpm and MChT xerogel/water-800 rpm samples (Table 3). Therefore, the maximal value of \(∆λ\) and the minimal value of \(E_g\) were obtained for the sample milled in water at 800 rpm. It is important that \(E_g\) for some modified samples is lower than 3.26 eV. The latter is a necessary condition for photocatalytic activity at visible light [38].

### Photocatalytic properties

The treatment methods (MChT, MWT) used in the discussed materials resulted in an increase in photocatalytic activity in the UV range compared to the iniZrO\(_2\). This is evidenced by the values of the rate constants for the rhodamine B \(K_d\) (UV) degradation (Table 3). The photodegradation rate constants \(K_d\) were calculated from the slopes of the plots ln(\(D/D_0\)) – \(t\) (where \(D\) and \(D_0\) are the values of optical density of RhB solution after time \(t\) and dark adsorption, respectively) using the first-order kinetic equation [8, 38, 39]. As can be seen, the initial ZrO\(_2\) sample showed low activity but its modification promotes enhancement of photocatalytic activities. The greatest UV activity was observed for the MChT xerogel/water-800 rpm. In this case, the value of \(K_d\) was 9.4 \(×\) 10\(^{-5}\) s\(^{-1}\) (Table 3). As mentioned above, a shift of the absorption edge toward larger wavelengths and narrowing a band gap was observed also for the modified samples (Fig. 7). Just the MChT xerogel/water-800 rpm sample has a minimum value of \(E_g\). It is interesting that the reference commercial photocatalyst P-25 (TiO\(_2\) composed of anatase and rutile) [25, 38] exhibited higher activity than iniZrO\(_2\) but lower activity compared with some modified samples of ZrO\(_2\). The larger bandgap for P-25 is the main reason for this.

On the other hand, the initial sample of ZrO\(_2\) is photocatalytically inactive in the visible region due to its high-value

| Samples          | \(t_{endo}\)  | \(t_{exo}\)  | \(Δm_{20–200}\) | \(Δm_{200–500}\) |
|------------------|---------------|---------------|----------------|-----------------|
| iniZrO\(_2\)     | 110; 130      | 436           | 21.7           | 6.4             |
| MChT gel-600 rpm | 90; 170       | 427           | 10.7           | 6.5             |
| MWT gel-190 °C   | 115           | 397; 473      | 7.7            | 7.2             |

Table 2 The results of thermal analysis for the exemplary samples

| Sample                  | \(λ\) nm | \(E_g\) eV | \(K_d\) \(10^5\) (UV) s\(^{-1}\) | \(K_d\) \(10^5\) (Vis) s\(^{-1}\) |
|-------------------------|----------|------------|---------------------------------|---------------------------------|
| iniZrO\(_2\)            | 268      | 4.63       | 2.2                             | –                               |
| MChT gel-800 rpm        | 401      | 3.09       | 8.8                             | 6.2                             |
| MWT gel-190 °C          | 376      | 3.31       | 7.0                             | 2.6                             |
| MChT xerogel/air-300 rpm| 363      | 3.42       | 5.7                             | 1.2                             |
| MChT xerogel/water-300 rpm| 325    | 3.85       | 3.1                             | 0.3                             |
| MChT xerogel/water-800 rpm| 405     | 3.06       | 9.4                             | 5.0                             |
| P-25                    | 376      | 3.30       | 6.1                             | 1.1                             |

Table 3 The electronic characteristics and photocatalytic activities of some ZrO\(_2\) samples

![Fig. 7 The UV–VIS diffuse reflectance spectra for the ZrO\(_2\) samples](image-url)
Even more important is the fact that modified ZrO\textsubscript{2} becomes photocatalytically active under visible illumination and more active than the reference titanium dioxide P-25.

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Conclusions

The MChT and MWT affect the crystalline structure of ZrO\textsubscript{2} to varying degrees: they do not change its X-ray amorphous state in the former case and promote the formation of a monoclinic phase already at 150–190 °C in the latter case. A more open, namely meso-macroporous structure is formed in both cases. As a result, the specific surface area increases by 25% when gels are subjected to MWT and more than twice when gels are milled. A bi-porous structure is formed in the latter case. It is important that the structure transformations are accompanied by significant changes in electronic characteristics of modified ZrO\textsubscript{2}: the absorption edge is shifted toward the visible region. The latter results in significant narrowing the band gap. Therefore, zirconium dioxide after MChT and MWT is characterized by a higher photodegradation rate of rhodamine B at the UV irradiation. Even more important is the fact that modified ZrO\textsubscript{2} becomes

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