

Research Article

Influence of Nd-Doping on Photocatalytic Properties of TiO₂ Nanoparticles and Thin Film Coatings

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Structural, optical, and photocatalytic properties of TiO₂ and TiO₂:Nd nanopowders and thin films composed of those materials have been compared. Titania nanoparticles with 1, 3, and 6 at. % of Nd-dopant were synthesized by sol-gel method. Additionally, thin films with the same material composition were prepared with the aid of spin-coating method. The analysis of structural investigations revealed that all as-prepared nanopowders were nanocrystalline and had TiO₂-anatase structure. The average size of crystallites was ca. 4-5 nm and the correlation between the amount of neodymium and the size of TiO₂ crystallites was observed. It was shown that the dopant content influenced the agglomeration of the nanoparticles. The results of photocatalytic decomposition of MO showed that doping with Nd (especially in the amount of 3 at. %) increased self-cleaning activity of the prepared titania nanopowder. Similar effect was received in case of the thin films, but the decomposition rate was lower due to their smaller active surface area. However, the as-prepared TiO₂:Nd photocatalyst in the form of thin films or nanopowders seems to be a very attractive material for various applications.

1. Introduction

The removal of inorganic and nonbiodegradable organic compounds is a crucial ecological problem. Dyes are an important class of synthetic organic compounds used mainly in the textile industry and therefore they are common industrial pollutants. Since the discovery of synthetic products, the global amount of dyes has been increasing year by year. Water wastes generated by the textile industry are known to contain considerable amounts of nonfixed dyes and azo dyes. Around 15% of the total world production of dyes is lost during the dyeing process and is released in textile effluents [1]. The release of those colored compounds into the ecosystem is a dramatic source of esthetic pollution and of perturbations in the aquatic life. Unfortunately, for the environment, they are very stable molecules and many efforts must be carried out for their decomposition [2].

Photocatalysis was well described in the literature [3–10]. Degradation of pollutants is a consequence of oxidation and reduction reactions due to photo-generation of charge carriers (electron-hole pairs) [3, 11–18]. There are a lot of materials that could be considered as effective photocatalysts, for example, ZnO [19], ZrO₂ [20, 21], CdS [22], MoS₂, Fe₂O₃, and WO₃ [3, 11–14]. However, the most widely used is titanium dioxide. Titania can be manufactured in a form of, for example, various kinds of layers, nanoparticles, nanotubes, solutions, or gels [14]. Photocatalytic activity of TiO₂ is related to many factors such as the method of preparation, amount and type of dopant, crystalline structure, surface properties, surface area, density of surface OH⁻ group, and parameters of postprocess treatment (e.g., temperature of annealing) [23]. One of the ways to increase its photocatalytic activity is manufacturing TiO₂ in the nanocrystalline form because the crystallite size reduction has a positive effect on this property

[24, 25]. Numerous scientific works have studied the effect of titania structure modification on photocatalysis [26, 27], for example, materials with the two-phase structure (anatase-rutile) [28, 29]. Another way to improve the self-cleaning properties of TiO_2 is doping, for example, with lanthanide ions having 4f configuration, such as Nd, Eu, or Tb [29–39]. Among them, neodymium doping has attracted considerable interest due to comparatively large size of Nd^{3+} ion, which causes a localized charge perturbation during substitutional doping into TiO_2 -lattice to increase its photocatalytic activity [40, 41]. Usually, higher activity of Nd-doped materials can be explained by the electronic character of neodymium with the partially filled atomic *d* or *f* shells [42]. The absorption of equivalent energy during UV-Vis light exposure results in electron excitation and transition from $\text{Nd}^{3+} 4f^3$ orbital. The surrounding of Nd^{3+} can react with Nd^{4+} ions obtained from the self-sensitization process and form the positively charged neodymium clusters (Nd_m)^{m+} ($m > 3n$). Nd-clusters have empty energy levels (subbands) below the conduction band of TiO_2 (Figure 1). Therefore, the charge transfer from the TiO_2 matrix to the empty Nd^{3+} levels may occur [42]. Such transition requires less energy than the transfer valence-conduction band in TiO_2 and can also proceed in the visible light [43]. The schematic representation of the photo-induced process of pollutant decomposition is shown in Figure 1. According to authors of previous works [39], the photo-induced electrons are transferred to $^4F_{3/2}$ level of Nd^{3+} ions via matrix defect states (DS), which are located below the titania conduction band. The authors suggest that electrons from neodymium energy levels or from DS are trapped (EC: electron capturing) by O_2 (acceptors) which results in the creation of superoxides $\text{O}_2^{\cdot -}$ (radical anions) that participate in the formation of hydroxyl radicals (OH^{\cdot}). During the light exposure also holes (positively charged vacancies) are created in the TiO_2 valence band. They are responsible for the extraction of electrons from water and hydroxyl species to produce OH^{\cdot} , which oxidizes (decomposes) dye molecules on the surface. The phenomenon of higher photocatalytic activity of Nd-doped nanomaterials can be explained as a higher efficiency of indirect energy transfer from the conduction band of TiO_2 to O_2 via DS or energy levels of Nd^{3+} and higher number of oxygen vacancies in DS near the valence band of TiO_2 . Both phenomena are responsible for creation of OH^{\cdot} that fulfill a key role in the decomposition process.

Similar conclusions about photocatalytic activity of TiO_2 :Nd were presented in the works by Hewer et al. [29], Wang et al. [44], Shah et al. [45], and Li et al. [46]. The authors suggested that ions of Nd-dopant can act as electron and/or hole traps. This kind of traps may decrease the recombination rate of e^-/h^+ pairs and therefore it may increase the lifetime of charge carriers, which causes that the photocatalytic activity is more efficient [29]. An explanation of the effect of neodymium dopant on the photocatalytic activity of titania requires a consideration of the role of Ti–O–Nd bonds in the mechanism of indirect transfer of photo-generated carriers. According to Hewer et al. [29] these bonds are created on the surface of the TiO_2 nanocrystals in the

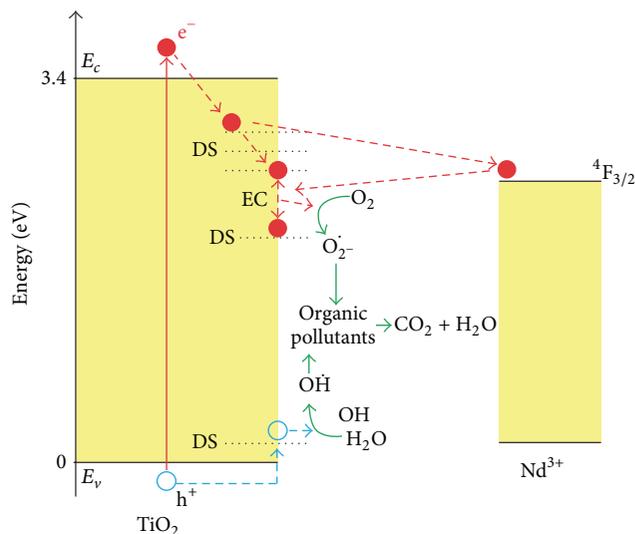


FIGURE 1: Schematic representation of photo-induced decomposition of organic pollutants with TiO_2 :Nd. Designations: EC: electron capturing, DS: defect states, e^- : electron, h^+ : hole, E_c : conduction band, and E_v : valence band.

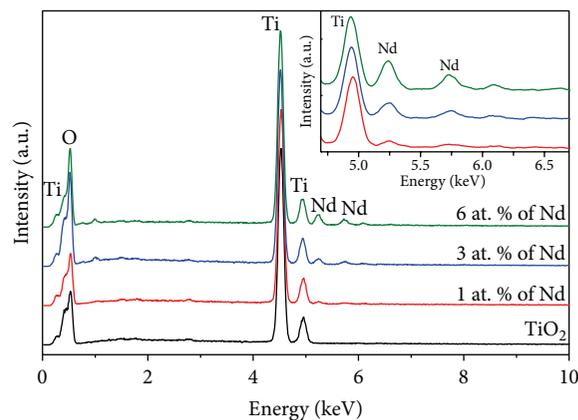


FIGURE 2: EDS spectra of TiO_2 nanoparticles doped with different amounts of neodymium.

surrounding of Nd_2O_3 . Our earlier research on thin film coatings based on TiO_2 :Nd also showed that Nd^{3+} ions were probably located on the surface of TiO_2 nanocrystallites in a form of small Nd_2O_3 agglomerates [39]. Similar conclusions were also presented in other works [29, 33–35]. Moreover, our previous investigations on TiO_2 thin films doped with lanthanides (Tb and Nd) showed that very effective direct and/or indirect energy transfer of excited electrons may occur due to such location of RE-oxides agglomerates [39, 47]. In case of TiO_2 :Nd, the energy levels of titania matrix are localized above $^4F_{3/2}$ level of Nd^{3+} . Therefore, an increase in the titania DS would probably have a positive impact on the photocatalytic efficiency of TiO_2 :Nd due to more probable indirect transitions. Moreover, as reported by Kralchevska et al. [33], the formation of RE clusters with discrete empty multienergy levels below the conduction band of TiO_2

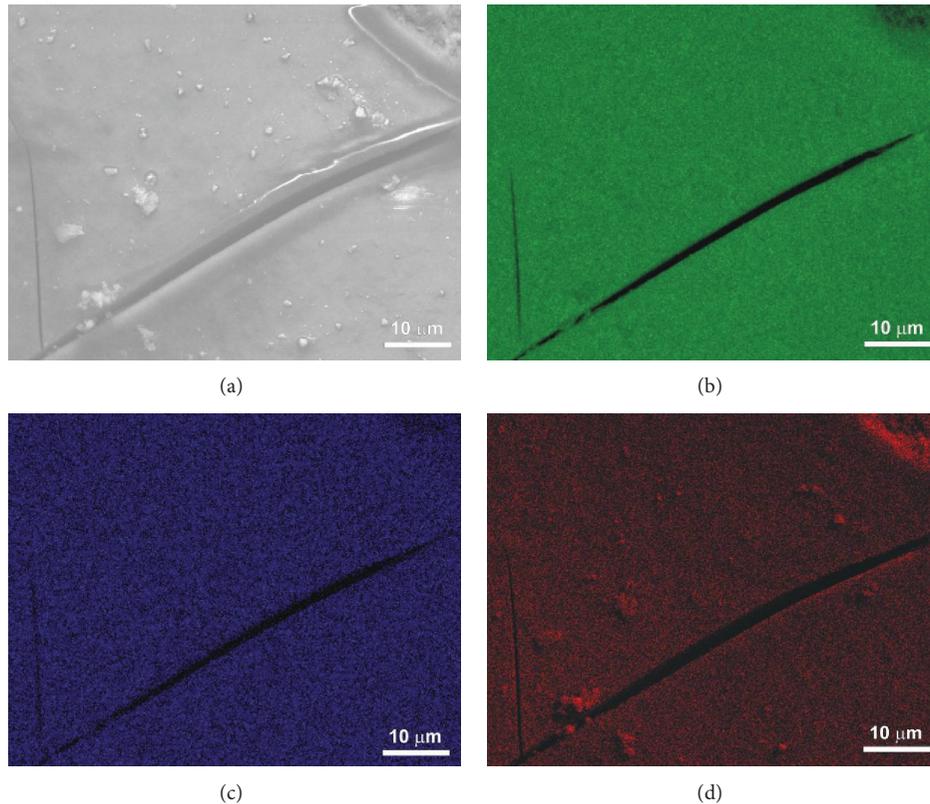


FIGURE 3: Results of X-ray microanalysis: (a) secondary electron image of selected area of $\text{TiO}_2\text{:Nd}$ (3 at. %), (b) Ti, (c) Nd, and (d) O elements concentration distribution.

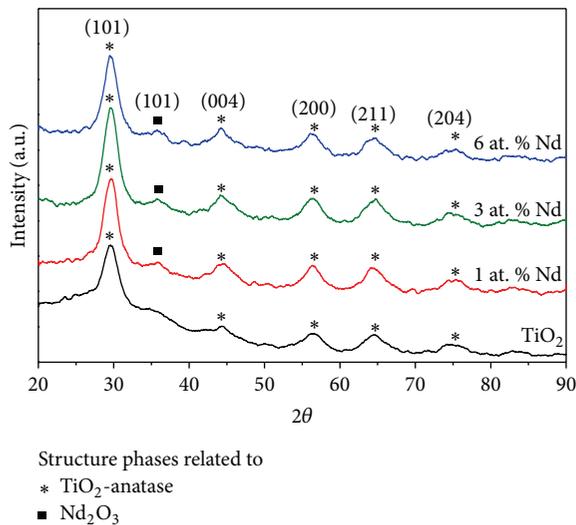


FIGURE 4: XRD patterns (Co $K\alpha$ radiation) of TiO_2 and $\text{TiO}_2\text{:Nd}$ nanoparticles prepared by sol-gel method.

allows transitions from the titania valence band to these levels. Thanks to this process, the ability of visible light absorption by titania increases, which results in slightly better performance of Nd-doped catalyst under solar irradiation. According to Yang et al. [34], certain amount of Nd_2O_3 on

the surface of TiO_2 results in more efficient separation of charge carriers, prolongation of their lifetime, and inhibition of the recombination process. However, when the Nd-dopant content exceeds a certain level, an excessive amount of Nd_2O_3 on the surface of titania would inhibit the adsorption of the dye and decrease the light absorption, thus decreasing the photocatalytic activity. From this reason, titanium dioxide doped with an adequate amount of neodymium could have higher photocatalytic activity and would be much better suited to the role of commercial photocatalyst as compared to undoped TiO_2 .

In this study, undoped and neodymium doped titanium dioxide nanoparticles were synthesized by sol-gel method. As-prepared samples were used for the photocatalytic degradation of the methyl orange (MO). Additionally, the thin films were prepared using spin-coating method and their photocatalytic properties were also determined in order to compare self-cleaning activity of prepared nanoparticles and thin films.

2. Experimental

Chemical reagents and solvents used in this study were of analytical or reagent grade and used as received, without further purifications. In a typical synthesis, 75 mL of (acidic) distilled water (pH = 1, adjusted with nitric acid, Baker, 65%, $d = 1.40 \text{ g/mL}$) was added dropwise to 2 mL of

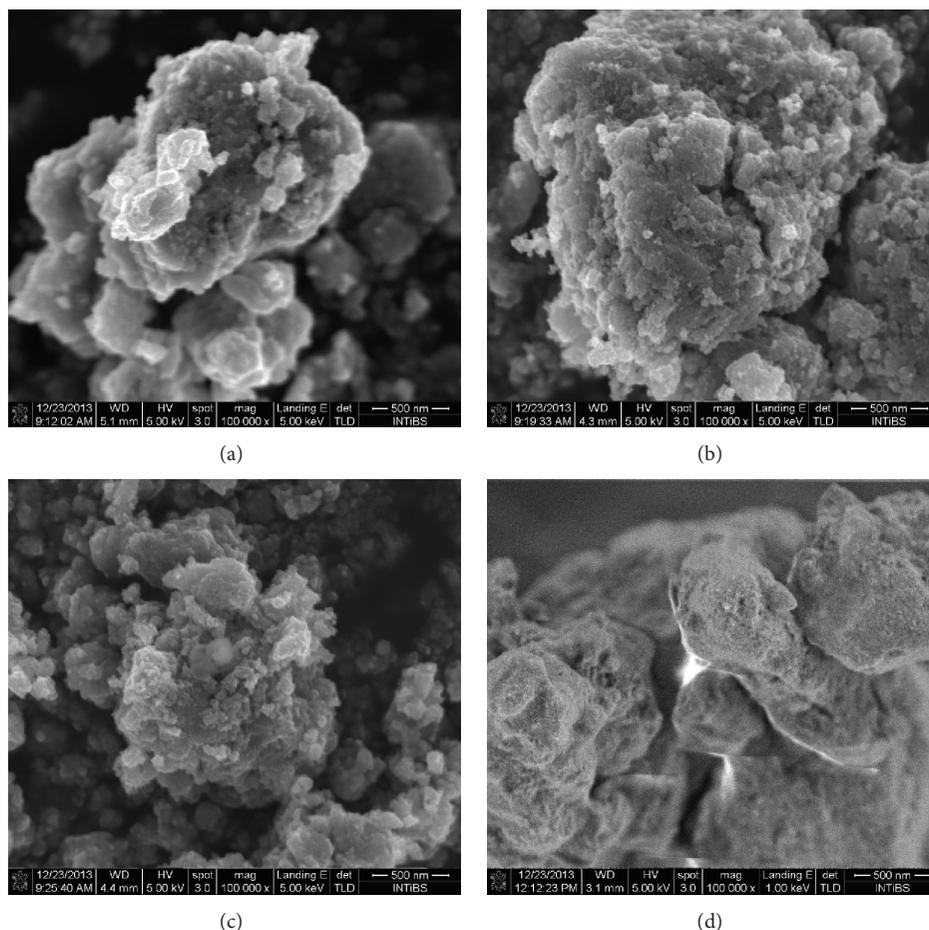


FIGURE 5: SEM images of (a) TiO_2 , (b) $\text{TiO}_2\text{:Nd}$ (1 at. %), (c) $\text{TiO}_2\text{:Nd}$ (3 at. %), and (d) $\text{TiO}_2\text{:Nd}$ (6 at. %) nanoparticles.

titanium tetraisopropoxide (TTIP, Sigma Aldrich, $\geq 98\%$, $d = 0.96 \text{ g/mL}$), dissolved in 25 mL of 2-propanol (Lab-Scan, $\geq 99.7\%$, $d = 0.78 \text{ g/mL}$) under vigorous magnetic stirring and heated at 80°C for 6 hours. Hydrolysis of titanium precursor occurred immediately, as indicated by the appearance of white turbidity. This resulted in a transparent translucent/milky-white colloidal system with a TiO_2 concentration of about 5 g/L (stable for several days at room temperature, without coagulation): $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4(\text{CH}_3)_2\text{CHOH}$. The colloidal solution was dried in an oven in air atmosphere. This led to the formation of a white/yellowish powder. Finally the samples were annealed at 120°C for 2 hours in air for further characterization and MO photocatalytic degradation. Neodymium doped TiO_2 nanoparticles were prepared using modified version of the above procedure. An appropriate amount of pure neodymium salt ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was added to obtain a doping level of 1.0, 3.0, and 6.0 at. % (nominal atomic concentration based upon the assumption of quantitative incorporation of the dopants).

Structural properties of synthesized TiO_2 and $\text{TiO}_2\text{:Nd}$ nanoparticles were determined based on the results of the

X-ray diffraction (XRD) method. For the measurements, Siemens 5005 powder diffractometer with $\text{Co K}\alpha$ X-ray ($\lambda = 1.78897 \text{ \AA}$) was used. The XRD studies were performed using Co lamp filtered by Fe (30 mV, 25 mA) and step size was equal to 0.02° of/in 2θ range, while time-per-step was 5 s. The correction for the broadening of the XRD instrument was accounted and the crystallite sizes were calculated using Scherrer's equation [49].

The surface morphology of the thin films was investigated with the aid of a FESEM FEI Nova NanoSEM 230 scanning electron microscope (SEM) with 30 kV of acceleration voltage. Moreover, this system was equipped with EDAX EDS microanalyzer for investigation of material composition.

High resolution transmission electron microscopy (HRTEM) as well as selected area electron diffraction (SAED) studies was performed using a Philips CM20 SuperTwin transmission electron microscope with 200 kV of acceleration voltage, which provided a resolution of 0.24 nm. A drop of each TiO_2 and $\text{TiO}_2\text{:Nd}$ (3 at. %) nanopowders (suspension in methanol) was loaded on carbon coated copper grids and dried under a lamp. Average size of TiO_2 and $\text{TiO}_2\text{:Nd}$ (3 at. %) crystallites was calculated from TEM

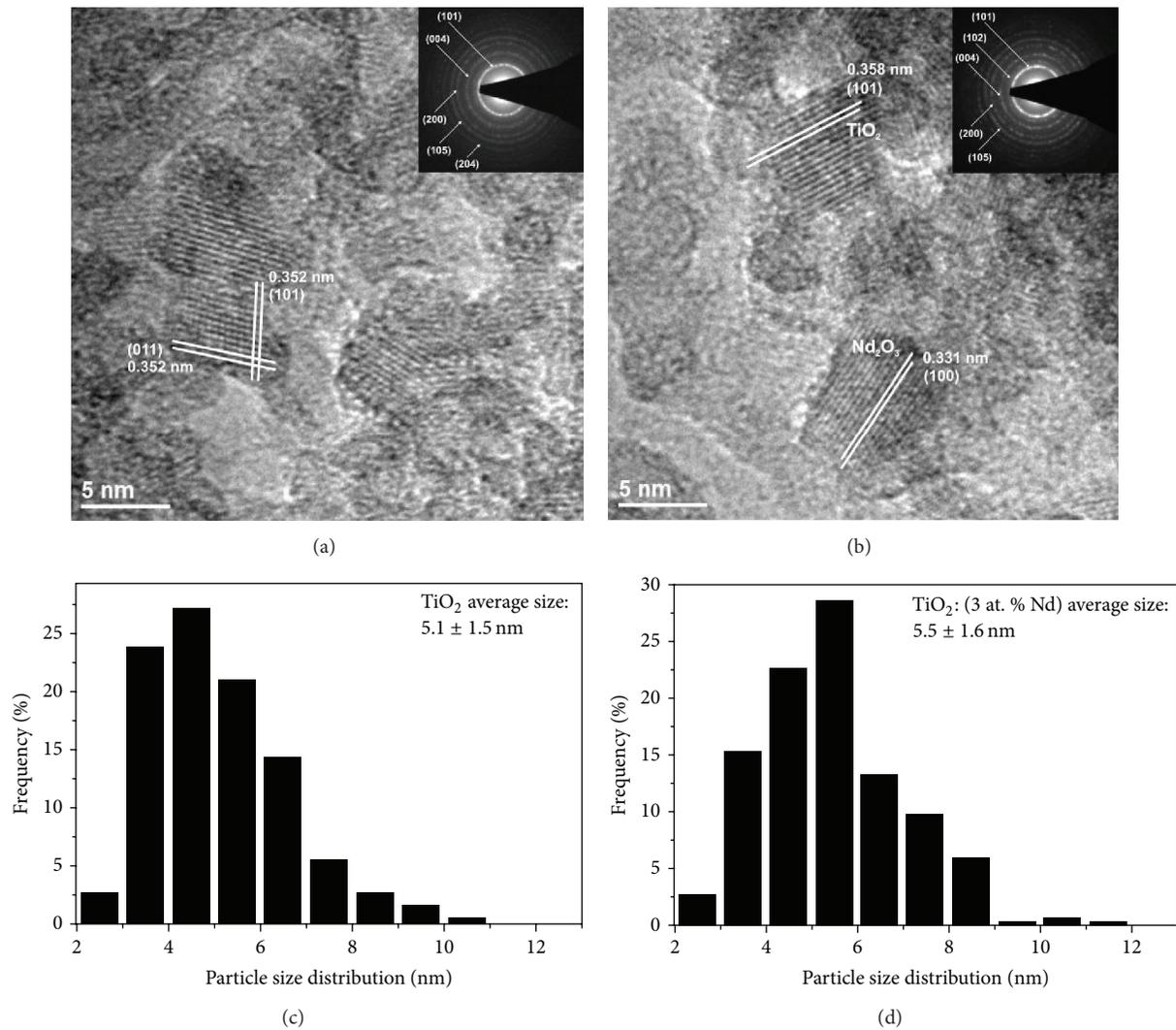


FIGURE 6: HRTEM images and particles size distribution of (a) TiO_2 and (b) $\text{TiO}_2\text{:Nd}$ (3 at. %) nanoparticles.

images with the aid of ImageJ program [50]. Received values were obtained based on about two hundred particles in each case.

The influence of neodymium doping on photocatalytic properties of nanocrystalline TiO_2 nanoparticles was estimated based on methyl orange decomposition reaction. The experimental setup consisted of a UV-Vis light source (6×20 W Phillips lamps with intensity of UV and Vis radiation: 183 W/m^2 and 167 W/m^2 , resp.) and cylindrical reservoir, which contained 200 mL of solution with MO concentration of 25 mg/L and 100 mg of the photocatalyst. To avoid the heating of the solution, the reaction temperature was controlled by circulation of water through the jacket at a constant temperature of ca. 15°C . All experiments were carried out under agitation with a magnetic stirrer, operating at 500 rpm, in order to provide a good mixing of the suspension. No external oxygen supply was used. No measurable degradation of the methyl orange occurred in the absence of TiO_2 nanoparticles. 30 minutes of premixing at a constant temperature in a dark condition was enough to achieve an

adsorption/desorption equilibrium and after that time the light was switched onto initiate the reaction. To determine the change in MO concentration, the samples containing its solutions were withdrawn from the reactor regularly every 60 minutes for 5 hours. The solutions were poured into a quartz cuvette and analyzed by OceanOptics QE 65000 UV-Vis spectrophotometer coupled with Mikropack DH-2000-BAL deuterium-halogen light source, in the wavelength range of 300–700 nm. MO concentration was calculated from the absorption peak at ca. 466 nm by means of a calibration curve.

In this study, TiO_2 and $\text{TiO}_2\text{:Nd}$ thin films were additionally manufactured with the aid of spin-coating method. The coatings were deposited using previously prepared solutions by sol-gel technique on Corning 7059 type substrates. For this purpose, a Spincoat SCS G3P-8 centrifuge was used. All samples (twice coated substrates) were dried at 120°C for 2 hours. The photocatalytic activity of thin films was also examined and the test procedure was the same as in the case of nanopowders. Surface morphology of manufactured coatings

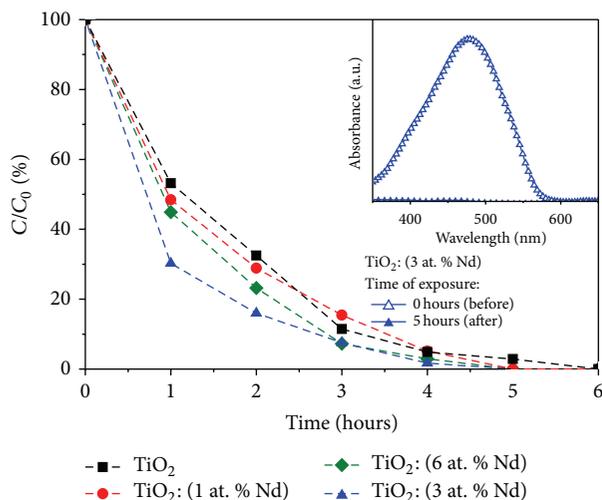


FIGURE 7: Photocatalytic activity of TiO_2 and $\text{TiO}_2\text{:Nd}$ (1, 3, and 6 at. % of neodymium) nanoparticles after exposure to the UV-Vis light. Designations: C_0 : initial concentration and C : concentration of methyl orange after time t .

was investigated with the aid of optical profiler Talysurf CCI Lite (Taylor Hobson), while the optical properties were determined on the basis of transmittance spectra in the wavelength range of 300 to 1000 nm.

3. Results and Discussion

3.1. Material Composition. Material composition of nanoparticles was measured using energy dispersive spectroscopy and the amount of neodymium dopant was in a good correlation with the quantitative assumption. The amount of dopant was ca. 1, 3, and 6 at. % (Figure 2). Results of X-ray microanalysis (Figure 3) show that the concentration distribution of each investigated element (Ti, Nd, and O) is homogenous. The area of investigation was ca. $50 \mu\text{m} \times 65 \mu\text{m}$.

3.2. X-Ray Diffraction of Nanopowders. XRD results of undoped and neodymium doped TiO_2 nanoparticles are shown in Figure 4. Broad peaks which are present in the patterns testify the nanocrystalline anatase structure of prepared samples. The average size of crystallites is in the range of 4.2 to 4.6 nm for TiO_2 and $\text{TiO}_2\text{:}(6 \text{ at. \% Nd})$, respectively. The doping of titanium dioxide with neodymium caused an increase in the crystallites sizes. Similar effect was observed by Khalid et al. [51], where a change in the amount of neodymium from 0.6 to 2 at. % resulted in an increase in the TiO_2 -anatase nanoparticles sizes from 7 to 13 nm, respectively. However, TiO_2 doping with neodymium can also give opposite results. According to Bokare et al. [52], an increase in the amount of Nd-dopant resulted in the decrease in the sizes of $\text{TiO}_2\text{:Nd}$ nanoparticles. In the XRD patterns of doped TiO_2 (Figure 4), a broad and very weak peak at 35.9° of 2θ range is observed. This peak is the strongest reflex from the hexagonal Nd_2O_3 -structure. The difference in ion radiuses (1.13 nm for Nd^{3+} and 0.64 nm for Ti^{4+}) suggests

that the neodymium ion is unable to effectively incorporate into the crystal lattice position of TiO_2 . Therefore, it is more reasonable to assume that Nd-containing particles are localized at the surface of TiO_2 nanocrystals.

3.3. SEM Investigations of Nanoparticles. SEM images obtained for the prepared nanoparticles (Figure 5) show that undoped titania nanoparticles formed agglomerates, whose shape and size are irregular. It seems that for TiO_2 doped with neodymium in the amount of 1 at. % and 3 at. % the agglomerates are a bit smaller. Incorporation of the neodymium dopant in the amount of 6 at. % resulted in a significant change in morphology of the grains. Similar results of SEM investigations of TiO_2 and $\text{TiO}_2\text{:Nd}$ (1 at. %) were obtained by Bokare et al. [52]. According to those studies, undoped titanium dioxide nanoparticles had irregular shapes and various sizes of the grains. In case of doping with neodymium Bokare et al. obtained nanoparticles with more uniform shape and size.

3.4. TEM Investigations of Nanoparticles. HRTEM images with SAED insets of TiO_2 and $\text{TiO}_2\text{:Nd}$ (3 at. %) nanoparticles are shown in Figure 6. All diffraction rings on both SAED patterns correspond to the TiO_2 -anatase structure. Figure 6(a) presents pure TiO_2 nanoparticles with marked (0 1 1) and (1 0 1) planes. For $\text{TiO}_2\text{:Nd}$ (3 at. %) nanopowder (Figure 6(b)) the TiO_2 and Nd_2O_3 nanoparticles can be observed. The values of lattice distances 3.58 Å and 3.31 Å correspond to (1 0 1) plane of TiO_2 -anatase and (1 0 1) plane of Nd_2O_3 structure, respectively. Particles size distributions of pure and doped TiO_2 are similar and in the range of 2–12 nm (Figure 6). The average sizes of nanoparticles are 5.1 nm and 5.5 nm for TiO_2 and $\text{TiO}_2\text{:Nd}$ (3 at. %) samples, respectively. These sizes are in good agreement with XRD results (Figure 4, Table 1).

Results of TEM investigation by Bokare et al. [52] also revealed that doped titania particles were small, but their shape was irregular. Moreover, the distribution of the nanoparticles size was in the range from 5 nm to 14 nm, while most of them were in size of 7–8 nm [52]. Additionally, TEM studies performed by Khalid et al. [51] revealed that the $\text{TiO}_2\text{:Nd}$ nanoparticles were homogenous in shape and their size was in the range of 8 nm to 12 nm. Presented studies showed that preparation of Nd-doped powder by sol-gel method enabled one to obtain nanocrystalline material with the particles of much smaller size than pure titania.

3.5. Photocatalytic Investigations of Nanopowders. The results of photocatalytic reactions showed that all nanopowders prepared by the sol-gel technique were active (Figure 7). Moreover, it was found that an appropriate amount of Nd-dopant had a beneficial effect on the level of MO decomposition by titania nanoparticles. In case of the nanopowder containing 3 at. % of neodymium the decomposition of the dye was the most dynamic and this sample had the highest photocatalytic activity. Slightly worse results were obtained for the $\text{TiO}_2\text{:}(6 \text{ at. \% Nd})$, $\text{TiO}_2\text{:}(1 \text{ at. \% Nd})$ and undoped TiO_2 , respectively. This means that there is an optimum amount of Nd-dopant,

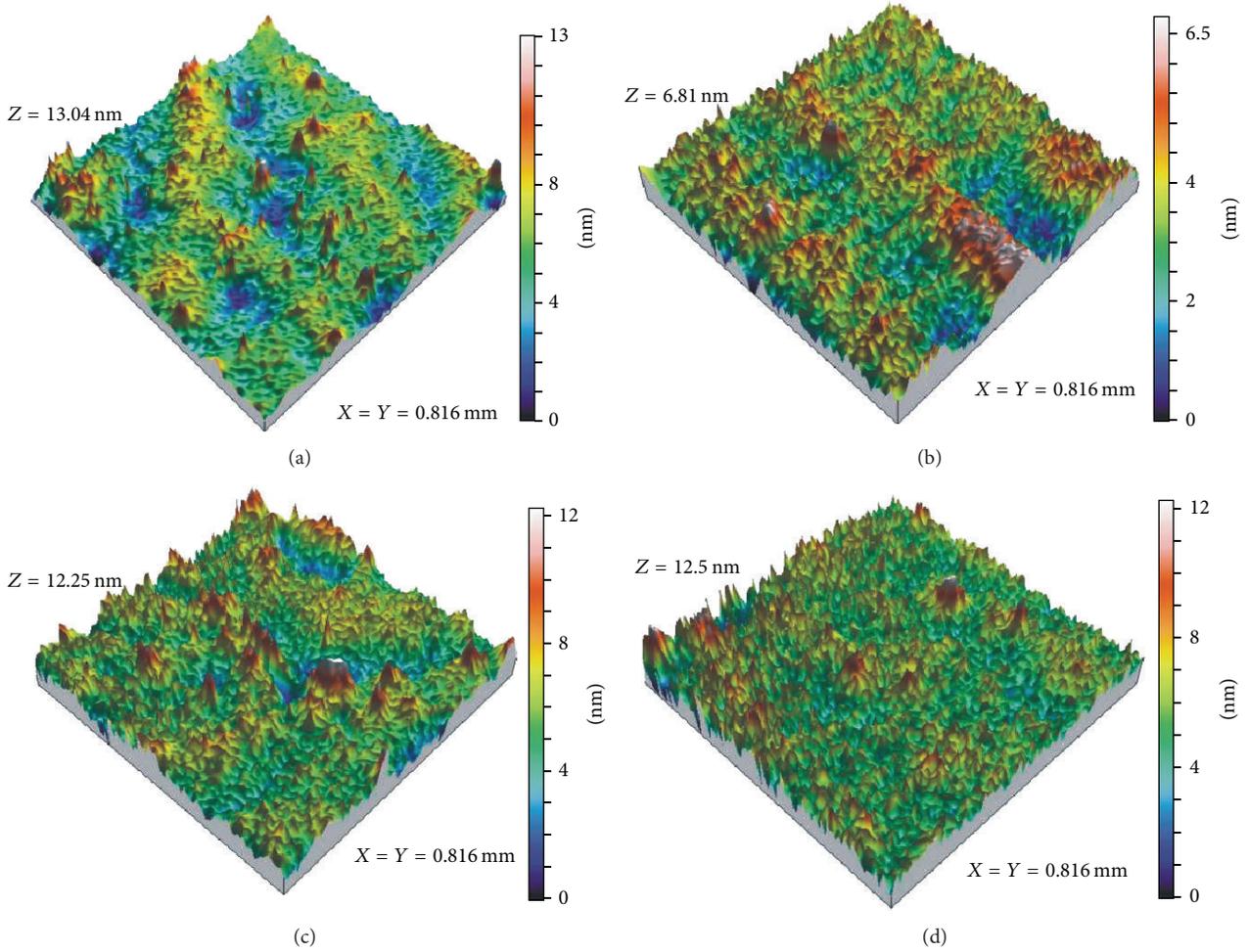


FIGURE 8: 3D surface topography profiles of prepared thin films: (a) TiO_2 , (b) TiO_2 :(1 at. % Nd), (c) TiO_2 :(3 at. % Nd), and (d) TiO_2 :(6 at. % Nd).

TABLE 1: Influence of Nd-dopant on structural parameters of titanium dioxide nanoparticles, based on XRD results.

Nanoparticles	Phase	(hkl)	2θ	d (nm)	d_{PDF} (nm)	D (nm)
TiO_2			29.59	0.3503		4.2
TiO_2 : Nd						
1 at. % Nd	Anatase	(101)	29.64	0.3497	0.3520 [48]	4.4
3 at. % Nd			29.62	0.3499		4.5
6 at. % Nd			29.58	0.3504		4.6

Designations: d : interplanar distance, d_{PDF} : standard interplanar distance, D : average crystallites size.

while too much Nd adversely affects the efficiency of MO decomposition. Similar effect was revealed by Bokare et al. [52], but, in case of their TiO_2 :Nd nanopowders, the optimal value of Nd was 1 at. %, which resulted in 30% higher activity of that nanopowder as compared to undoped one. Similar results were obtained by Khalid et al. [51]. In their studies 1 at. % of Nd was also an optimum value for the photocatalysis, but the efficiency of reaction was only 20% better than for pure titania.

We suggest that high activity of our powders was directly related to small size of nanoparticles, which were in the

range of ca. 4-5 nm (according to XRD and TEM results). Thanks to this fact, very large surface area per gram of the nanopowders was obtained. However, due to similar sizes of the nanoparticles their optimal size cannot be clearly determined. In our opinion the mechanism of indirect energy transfer via energy levels of neodymium ions fulfills a key role in heterogeneous photocatalysis phenomenon.

To exclude the possibility that the decoloration was caused by the UV-Vis light itself, some experiments were carried out without the photocatalyst. The differences in the UV-Vis spectra before and after irradiation for five hours were

negligible, which indicated that no decomposition of MO in the absence of TiO_2 nanopowders was observed or the rate of this reaction was very low.

3.6. Thin Films Investigations Results. Thin films were prepared from the same sol-gel solutions as the ones used for nanopowders manufacturing. Their photocatalytic activity was compared to nanoparticles. In Figure 8 three-dimensional (3D) surface profiles of the films are presented. These studies have shown that the prepared coatings are homogeneous. Their surface roughness (S_a , the arithmetic mean height of the film) is very small, in the range of 0.9 to 1.4 nm, so it means that the surface is very smooth. Moreover, based on the recorded transmittance spectra (Figure 9) one can observe that all prepared thin films are transparent. However, the doping of titanium dioxide with neodymium caused the decrease in the average transmittance from ca. 86% for TiO_2 to ca. 76% for TiO_2 :(6 at. % Nd). Additionally, it can be also observed that the doping with neodymium shifted the cutoff wavelength from ca. 293 nm to 304 nm for TiO_2 and TiO_2 :Nd (6 at. %), respectively. Therefore, the absorption edge of the TiO_2 :Nd thin films has been shifted towards visible light range, what means that these coatings could absorb light in the wider range.

Results of photocatalytic decomposition of methyl orange during the reaction carried out in the presence of thin films are shown in Figure 10. The results clearly indicate that all manufactured films are photocatalytically active. Much lower activity of the thin films (ca. 2% after 5 hours), as compared to the full decomposition of the dye which was obtained in the case of nanoparticles, is associated primarily with the significant difference between the active area of the films and the nanoparticles. Despite the diametrical difference between them, both types of the samples were made from nanoparticles of the same size. In case of nanopowders, active surface area is often given even in tens of square meters. On the contrary, thin films were deposited on substrates that had the area of 12 square centimeters. Therefore, decomposition efficiency in range of about 2.5% can be considered as successful. It is worth to emphasize that after photocatalysis the material from which the thin films were formed was still on the substrate to which it was applied. Therefore, such films would not create problems for the environment, which are associated with nanoparticles recovering from the solution.

4. Conclusions

The analysis of structural investigations revealed that all as-prepared powders were nanocrystalline and had anatase structure. According to XRD and TEM results the average size of crystallites was ca. 4-5 nm. The relation between the amount of neodymium and the size of TiO_2 crystallites was observed and an increase in Nd-content resulted in an increase in crystallites size. Moreover, the correlation between the amount of Nd-dopant and the agglomeration level of nanoparticles was observed. Thanks to Nd-doping, the efficiency of photocatalytic decomposition of MO dye was considerably increased. The optimum amount of the dopant

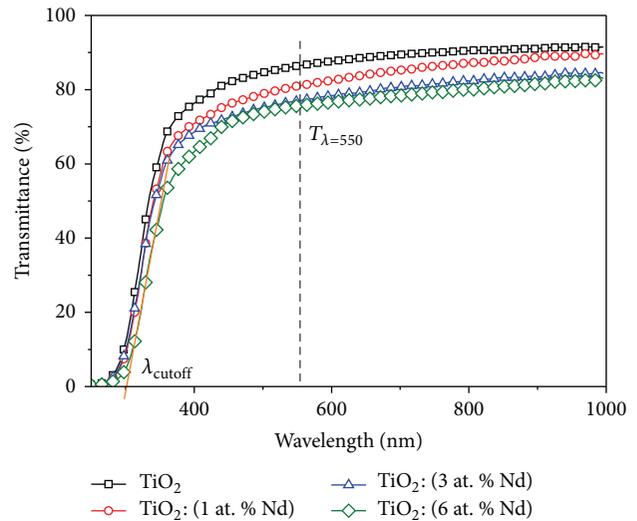


FIGURE 9: Transmittance spectra of TiO_2 and TiO_2 :Nd thin films prepared by spin-coating method.

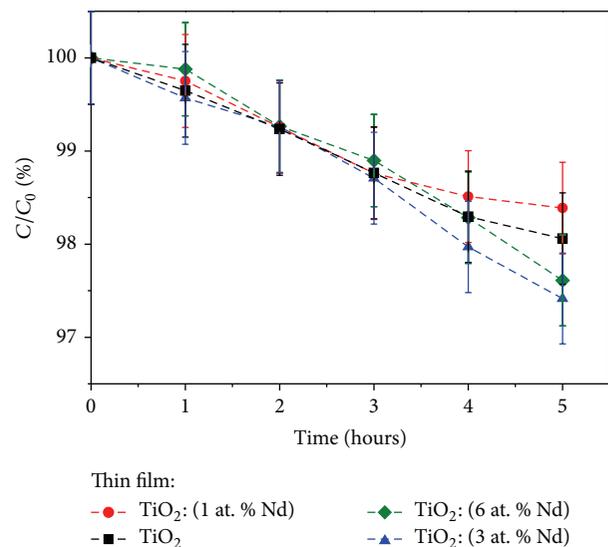


FIGURE 10: Photocatalytic activity of TiO_2 and TiO_2 :Nd (1, 3, and 6 at. % of neodymium) thin films after exposure to the UV-Vis light. Designations: C_0 : initial concentration and C : concentration of methyl orange after time t .

was established as 3 at. %. The dynamics of the reaction with this powder was the highest and after 4 hours the dye was completely decomposed. Similar effect was received in case of thin films prepared from the same material. However, due to their much smaller active surface area, as compared to the nanopowder, the decomposition rate was much lower. These results seem to be quite promising in spite of some disadvantages because as-prepared thin film coatings have high transparency in visible light range and very smooth surface with the roughness of ca. 1 nm. This means that such photocatalytically active material could find application as a

self-cleaning coating but in a form of a nanopowder it is also very attractive.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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