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# Preparation and photocatalytic activity of Nd-modified TiO<sub>2</sub> photocatalysts: Insight into the excitation mechanism under visible light

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#### ABSTRACT

Titanium dioxide (TiO<sub>2</sub>) nanoparticles (NPs) modified with neodymium (Nd) in the range between 0.1 and 1.0 mol% were prepared via the hydrothermal method. The samples obtained were characterized by diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), X-ray fluorescence (EDX), Brunauer-Emmett-Teller (BET) method, X-ray powder diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS) and photoluminescence spectroscopy (PL). The photocatalytic activity of the obtained samples was evaluated by photodegradation of phenol in aqueous solution under ultraviolet-visible (UV-Vis,  $\lambda$  > 350 nm) and visible (Vis,  $\lambda$  > 420 nm) irradiation. Experimental results showed that the photocatalysts exhibited high photocatalytic activity under Vis light. The sample showing the highest photoactivity under Vis irradiation was in the form of anatase; its surface area equalled  $124 \text{ m}^2/\text{g}$  (1.16 times larger than that of pristine TiO<sub>2</sub>). The average crystal size was 10.9 nm, and it was modified with 0.1 mol% of Nd<sup>3+</sup> (28% of phenol was degraded after 60 min of irradiation). The photocatalytic tests of phenol degradation in the presence of scavengers confirm that  $e^-$  and  $O_2^{\bullet-}$  were responsible for the visible light degradation of organic compounds in the aqueous phase. Action spectra analysis revealed that although Nd-modified TiO<sub>2</sub> could be excited under visible light in the range of 400-480 nm, the up-conversion process is not responsible for the degradation of phenol under Vis irradiation. © 2017 Elsevier Inc. All rights reserved.

### 1. Introduction

In recent years, various photocatalytic processes have been the subject of intensive research because they belong to the most sustainable and environmentally friendly technologies [1]. Titanium dioxide (TiO<sub>2</sub>) is one of the most widely used semiconductors for photocatalytic applications. The greater interest in TiO<sub>2</sub> rests in the fact that it is cheap, non-toxic, chemically and photochemically stable and has a strong oxidation capacity [2]. However, despite the promising properties, anatase TiO<sub>2</sub> is sensitive only to UV light due to a wide band gap (3.2 eV). Therefore, its application is limited because the UV region represents only 3–5% of the entire solar spectrum [3]. Many studies have been performed to develop various modifications of TiO<sub>2</sub> to obtain photocatalysts sensitive to visible light ( $\lambda > 400$  nm) [4–10].

In particular, modification with rare earth (RE) metals, such as neodymium (Nd<sup>3+</sup>), has a positive effect on photocatalytic activity under visible light [11–14]. The beneficial influence on photocatalytic activity by titania modification with RE has been ascribed to the f-orbitals of RE ions that can complex with various Lewis bases (e.g., acids, alcohols, aldehydes, amines, and thiols) [15,16]. Thus, inclusion of rare earth ions into a TiO<sub>2</sub> matrix could provide means to concentrate the substrates at the semiconductor surface. Moreover, modification with RE ions improves the separation efficiency of photoinduced electron-hole pairs and prevents recombination [4].

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The effect of Nd modification on the photocatalytic activity of TiO<sub>2</sub> has been reported in the literature. Štengl et al. synthesized RE-doped TiO<sub>2</sub> materials by precipitation method. They reported that neodymium-doped TiO<sub>2</sub> showed the highest photoactivity under Vis irradiation for degradation of Orange II dye among other RE-TiO<sub>2</sub> photocatalysts (such as  $Pr^{3+}$ ,  $Ce^{3+}$ ,  $Ce^{4+}$ ,  $Eu^{3+}$ ,  $Sm^{3+}$ ,  $Gd^{3+}$  and  $La^{3+}$ ) [17]. Bokare et al. used Nd-TiO<sub>2</sub> materials, synthesized

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by the sol-gel method, for degradation of methyl orange dye in an aqueous solution under solar light irradiation. It was observed that the dopant amount affected the photocatalytic activity of the photocatalysts. Nevertheless, the use of organic dyes as a model compound should be avoided due to their absorption of visible light and photosensitization of TiO<sub>2</sub>, which results in a complex mechanism of dye degradation [18]. There are only a few papers reporting photodegradation of other organic compounds. For example, Gomez et al. tested photocatalytic activities of Nd-TiO<sub>2</sub> photocatalysts, prepared at mild temperature by microwave-assisted treatment, for the degradation of phenol and rhodamine B under UV-Vis irradiation. It was found that the best photocatalytic activity was obtained for an optimal Nd content of 0.06 mol%, resulting in complete degradation of phenol in 120 min [19]. Xie et al. used the chemical coprecipitation-peptization method to prepare Ndmodified TiO<sub>2</sub> nanoparticles. The experimental results indicated improved photocatalytic activity of Nd-TiO<sub>2</sub> for phenol photodegradation compared to that of pristine TiO<sub>2</sub> under visible light irradiation [20].

Although many studies have reported on Nd-modified  $TiO_2$ , there is no available information regarding the origin of an excitation mechanism of Nd-TiO<sub>2</sub> under visible light. Some studies have reported an interesting approach that the up-conversion process can be responsible for photocatalytic activity of other RE-TiO<sub>2</sub> systems under Vis light irradiation [21,22]. Nevertheless, up-conversion was not discussed as a contributor to an improved excitation mechanism of Nd-TiO<sub>2</sub>.

In the present work, we report the synthesis and photocatalytic activity of neodymium-modified TiO<sub>2</sub> photocatalysts prepared by the hydrothermal method. The photocatalytic properties of all of the samples under UV-Vis and Vis irradiation were investigated by monitoring the degradation reaction of phenol in the aqueous phase. To understand what type of oxygen species participate in the degradation mechanism, a hydroxyl radical test with terephthalic acid and the reactive oxygen species formation tests using benzoquinone, silver nitrate, ammonium oxalate and tert-butanol as scavengers were studied. The photocatalytic degradation pathway of phenol was also examined. To explain the possible mechanism of Nd-TiO<sub>2</sub> photocatalyst excitation under visible light, the action spectra measurements were investigated for select samples. For the first time, the effects of irradiation wavelength on apparent quantum efficiency have been studied by employing photodegradation of phenol as a model pollutant.

#### 2. Experimental section

#### 2.1. Materials

Titanium isopropoxide (97%, TIP) and Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.99%), used as titanium and neodymium sources, were purchased from Sigma–Aldrich, Poland. Isopropanol and nitric acid (65%) were purchased from STANLAB, Poland. Ethanol, phenol and terephthalic acid were purchased from POCh S.A, Poland. P25 from Evonik, Germany was used as a standard and for comparison of the photocatalytic activity. Deionised water (0.05  $\mu$ S) was used for all reactions and treatment processes. All the chemicals were used as received without further purification.

# 2.2. Preparation of Nd-TiO<sub>2</sub>

The hydrothermal method was used for the preparation of Nd-TiO<sub>2</sub> nanoparticles. In a typical procedure, 136 mL of TIP was dissolved in 136 mL of isopropanol. Then, a mixture of 4.8 mL of water, a certain amount of solid Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 4.8 mL of isopropanol and 1.6 mL of nitric acid were added to the TIP solution.

#### Table 1

Description and physicochemical characterization of Nd-TiO<sub>2</sub> photocatalysts.

Sample label	Assumed content of Nd <sup>3+</sup> (mol.%)	$S_{BET}\left(m^2/g\right)$	Crystallite size (nm)
$\begin{array}{l} TiO_2 \\ 0.1\%Nd-TiO_2 \\ 0.25\%Nd-TiO_2 \\ 0.5\%Nd-TiO_2 \\ 1.0\%Nd-TiO_2 \end{array}$	None	107	18.8
	0.1	124	10.9
	0.25	141	8.8
	0.5	146	6.8
	1.0	160	4.7

The mixture was stirred for 30 min at room temperature. After treatment at 120 °C for 4 h in a 200 mL autoclave (hydrothermal process), the as-obtained samples were separated by centrifugation, washed three times with deionised water and ethanol, and dried at 35 °C for 16 h. Finally, the samples were ground and calcined at 450 °C for 2 h in a muffle furnace under air atmosphere with a heating rate of 2 °C/min followed by grinding to obtain the Nd-TiO<sub>2</sub> powder. A description of the prepared photocatalysts is shown in Table 1.

#### 2.3. Characterization of Nd-TiO<sub>2</sub>

To characterize the photoabsorption properties of pristine and modified photocatalysts, the diffusive reflectance spectra (DRS) were recorded on a Shimadzu UV–Vis spectrophotometer (UV 2600) equipped with an integrating sphere.  $BaSO_4$  was used as the reference. The obtained absorption spectra were recorded in the range of 250–850 nm with a scanning speed of 200 nm/ min at room temperature. DRS were recorded and data were converted by Kubelka–Munk (K-M) function to obtain absorption spectra.

Nitrogen adsorption-desorption isotherms were carried out at -197 °C (liquid nitrogen temperature) using a Micromeritics Gemini V (model 2365). The surface area was determined according to the standard Brunauer, Emmet and Teller (BET) method. All samples were degassed at 200 °C prior to nitrogen adsorption measurements.

The morphology of Nd-TiO<sub>2</sub> was determined using a Bruker spectrometer-coupled Quantax 200 scanning electron microscope, and the images were captured at 3000-fold magnification.

X-ray diffraction (XRD) was used to determine and verify the crystalline structure of the obtained photocatalysts. XRD patterns were recorded on a Rigaku diffractometer (RINT Ultima+) equipped with a graphite monochromator using Cu K $\alpha$  radiation (40 kV tube voltage and 20 mA tube current). Measurements were performed in a 2 $\theta$  range of 5–90°. Based on the results obtained, the particle sizes of photocatalysts and XRD data were calculated using the Scherrer's equation.

The surface composition of the samples was investigated by Xray photoelectron spectroscopy (XPS) on a PHI 5000 VersaProbeTM (ULVAC-PHI) spectrometer with monochromatic Al K  $\alpha$  radiation (hv = 1486.6 eV). The high-resolution (HR) XPS spectra were collected by the hemispherical analyzer at a pass energy of 23.5 eV, an energy step size of 0.1 eV and a photoelectron take off angle of 45° with respect to the surface plane. The binding energy (BE) scale of all detected spectra were calibrated by normalizing the large C—C peak in the C 1s region to 284.6 eV. The HR XPS spectra were deconvoluted with Gaussian–Lorentzian-shaped profiles.

Photoluminescence (PL) properties in the range of 300–700 nm were measured on Perkin Elmer limited LS50B spectrophotometer equipped with a Xenon discharge lamp as an excitation source and an R928 photomultiplier as a detector. The spectra were recorded with an excitation wavelength of 315 nm directed on the sample surface at an angle of 90°. PL spectra in the range of 400–1000 nm were measured on a Princeton Instrument PIXIS:256E

Digital CCD Camera equipped with an SP-2156 Imaging Spectrograph and Opolette 355LD UVDM tunable laser as the excitation source. The spectra were recorded with an excitation wavelength of 350 nm.

Total Organic Carbon was carried using TOC analyzer Shimadzu TOC-L.

#### 2.4. Photocatalytic experiments

The photocatalytic properties of the obtained Nd-TiO<sub>2</sub> samples were determined in a two-reaction system, i.e., phenol decomposition under polychromatic UV–Vis and Vis irradiation. Furthermore, a hydroxyl radical test under UV–Vis and Vis irradiation using terephthalic acid was investigated and besides that the reactive oxygen species formation test under Vis irradiation using benzoquinone, silver nitrate, ammonium oxalate and tert-butanol as scavengers was also performed. Additionally, to calculate quantum efficiency (action spectra measurements), phenol decomposition was measured under monochromatic irradiation. The experimental procedures have been selected and described based on different types of photocatalytic set-up and geometric of photoreactors.

#### 2.4.1. Phenol decomposition under polychromatic irradiation

Polychromatic irradiation was carried out for two irradiation ranges, UV–Vis ( $\lambda$  > 350 nm) and Vis ( $\lambda$  > 420 nm), using a 150 W Mercury lamp (Heraeus) and 1000 W Xenon lamp (Oriel 66021), respectively. The experimental procedure under UV-Vis irradiation was as follows: the photocatalysts (7.5 mg) were suspended in phenol aqueous solution (15 mL,  $C_0 = 20 \text{ mg/L}$ ) in boron-silicon test tubes. The experimental procedure under Vis irradiation was as follows: Nd-TiO<sub>2</sub> powder (125 mg) was suspended in phenol aqueous solution (25 mL,  $C_0 = 20 \text{ mg/L}$ ) in a quartz photoreactor. After 30 min of mixing (550 rpm) and aeration  $(5 \text{ dm}^3/\text{h})$  in the dark, the suspension was irradiated with a cut-off spectrum of light. To avoid the stripping of the phenol the temperature of the suspension during photoirradiation was maintained at 10 °C using a thermostatically controlled water bath. Samples of a 0.5 mL reaction mixture were collected at regular time periods during irradiation and filtered through syringe filters ( $\emptyset = 0.2 \mu m$ ) to remove the suspended photocatalyst particles. Kinetics of phenol degradation byproducts and phenol concentration were determined by highperformance liquid chromatography (HPLC, Shimadzu). The HPLC system was equipped with a Kinetex C18 column  $(150 \text{ mm} \times 3 \text{ mm}; \text{ particle size of } 2.6 \,\mu\text{m}; \text{ pore diameter } 100 \,\text{\AA})$ and the SPD-M20 A diode array detector ( $\lambda = 205$  nm). The flow rate was maintained at 0.4 mL/min with a mobile phase composed of acetonitrile and water (7.5/92.5 v/v). The injection volume was 30 µL.

#### 2.4.2. Hydroxyl radical generation efficiency

Terephthalic acid can produce the fluorescent compound 2-hydroxyterephthalic acid by reaction with hydroxyl radicals. The experimental procedure is described in Section 2.4.1. The photocatalysts were suspended in terephthalic acid aqueous solution  $(C_0 = 5 \cdot 10^{-4} \text{ mol/L})$ . Samples of a 2 mL reaction mixture were collected after 60 min irradiation and filtered through syringe filters ( $\emptyset = 0.2 \mu m$ ) to remove the suspended photocatalyst particles. Fluorescence spectra were measured at room temperature using a Perkin Elmer limited LS50B spectrophotometer equipped with a Xenon discharge lamp as an excitation source and an R928 photomultiplier as a detector. The obtained solution was measured with the excitation wavelength of 315 nm.

## 2.4.3. Reactive oxygen species generation efficiency

To investigate the role of the reactive oxygen species in the photocatalytic process, the photocatalytic activity test in the water phase under Vis ( $\lambda > 420$  nm), irradiation was conducted in the presence of silver nitrate, ammonium oxalate, benzoquinone and tert-butanol as scavengers of e<sup>-</sup>, h<sup>+</sup>, O<sub>2</sub><sup>-</sup> and OH radicals, respectively. In this case, 'scavenger' water solution was added to the reactor together with phenol aqueous solution (C<sub>0</sub> = 20 mg/L; 1:1 v/v). The experimental procedure is described in Section 2.4.1.

# 2.4.4. Phenol decomposition under monochromatic irradiation (action spectra measurements)

Action spectra measurements were investigated for the selected photocatalyst. Photocatalyst powder (50 mg) was suspended in aqueous solution (5.0 mL) containing phenol ( $C_0 = 20 \text{ mg/L}$ ) and placed in a quartz cell and then irradiated at monochromatic wavelengths for 90 min ( $\lambda$  = 400, 420, 440, 460, 480, 500, 520, 540, 560 nm), 180 min ( $\lambda$  = 585, 645, 675, 745 nm) and 360 min  $(\lambda = 805 \text{ nm})$  using a diffraction grating-type illuminator (Jasco, CRM-FD) equipped with a 300 W Xenon lamp (Hamamatsu, C2578-02). The light intensity was measured using an optical power meter (HIOKI 3664). During the experiments, the reaction mixtures were continuously stirred. During the irradiation, every 30 min a portion (0.2 mL) of the reaction mixture was withdrawn with a syringe and subjected to HPLC. The wavelengthdependent apparent quantum efficiency was calculated as the ratio of the rate of electron consumption from the rate of benzoquinone generation to the flux of incident photons, assuming that two photons are required according to the stoichiometry of this reaction. The HPLC system was equipped with a WAKOSIL-II SC18 AR column (250 mm  $\times$  4.6 mm). The flow rate was maintained at 1 mL/ min with a mobile phase composed of acetonitrile, water and phosphoric acid (60/40/1 v/v/v) with a sample injection volume of 5 µL, and the detector was operated at 254 nm.

# 3. Results and discussion

#### 3.1. Diffuse reflectance spectroscopy

To investigate the photoabsorption properties of the obtained photocatalysts, the diffusive reflectance spectra (DRS) (of Ndmodified TiO<sub>2</sub> samples were investigated in the range of 250-850 nm, and the results are shown in Fig. 1. Pristine TiO<sub>2</sub> and P25 were used as the reference samples. All prepared photocatalysts were white powders. Each sample has a broad intense absorption below 400 nm, which can be attributed to charge-transfer related to electron excitation from the valence band to the conduction band in TiO<sub>2</sub> [23–25]. P25 and as-prepared pristine TiO<sub>2</sub> did not exhibit any absorption in the visible region. All modified and pristine TiO<sub>2</sub> showed a redshift of their absorption compared to that of P25. Moreover, compared with Nd-TiO<sub>2</sub>, unmodified TiO<sub>2</sub> has a stronger absorption edge shift towards a longer wavelength. This behaviour was described in other studies [4,12,26–29], and the blueshift in the present work may be ascribed to the increase in the band gap after modification of titanium dioxide. The probably reason for such a band gap energy increase was gradual movement of the conduction band of TiO2 above the first excited state of RE<sup>3+</sup>. Rare earth ions at the first excited state could interact with electrons of the conduction band of TiO<sub>2</sub>, which would consequently cause higher energy transfer from TiO<sub>2</sub> to RE<sup>3+</sup> ions. Furthermore, the blueshift can also be assigned to effective quantum size due to the decrease in the crystalline size [4]. Beyond that, it can be seen that there are absorption bands located at 520, 585, 745, 805 nm, which can be attributed to the transition from the  ${}^{4}I_{9/2}$  ground state to the excited states of the neodymium  ${}^{4}G_{7/2}$ ,  $^2K_{13/2}$  and  $^4G_{5/2},\,^2G_{7/2}$  and  $^4S_{3/2},\,^4F_{7/2}$  and  $^4F_{5/2},\,^2H_{9/2}$  [24,30,31]. This study showed that the intensity of neodymium absorption bands



Fig. 1. UV-Vis Kubelka-Munk absorption spectra of Nd-TiO<sub>2</sub> photocatalysts compared to those of pristine TiO<sub>2</sub> and P25.

increases with the amount of  $Nd^{3+}$ , which is in agreement with the available literature [24,29,32,33].

#### 3.2. X-ray diffraction and BET surface area

The crystalline phase of pristine  $TiO_2$  and Nd-modified  $TiO_2$ nanoparticles was determined by X-ray powder diffraction. The XRD patterns of samples are shown in Fig. 2. In all synthesized photocatalysts, the figure presents a group of lines at 20 values of 25.4°, 37.9°, 48.1°, 54.1°, 55.1°, 62.9°, 70.5° and 75.2°, which are attributed to the anatase phase. This means that the phase transformation of anatase to rutile did not occur despite the heat treatment at 450 °C. In addition, the diffraction peaks of Nd<sub>2</sub>O<sub>3</sub> are not observed in any of the as-prepared Nd-modified TiO<sub>2</sub> photocatalysts. This indicated that the content of Nd<sup>3+</sup> was too small for detection, crystallites were very small and highly dispersed, Nd<sup>3+</sup> was present in the form of an amorphous phase or as Nd<sup>3+</sup>



Fig. 2. X-ray diffraction patterns of pristine TiO<sub>2</sub> and Nd-TiO<sub>2</sub>.

ions adsorbed either on the titania surface or placed inside the titania lattice [4,26,34].

The specific surface area and crystallite size of pristine and Ndmodified TiO<sub>2</sub> photocatalysts are shown in Table 1. All Ndmodified samples showed a higher BET surface area than that of the pristine  $TiO_2$  sample (107 m<sup>2</sup> g<sup>-1</sup>). The surface area varied from 124 to 160 m<sup>2</sup> g<sup>-1</sup>. An increase in the neodymium content from 0.1 to 1.0 mol% caused an increase in the BET surface area. The average crystallite size of anatase was calculated using the Scherrer equation and ranged from 4.7 to 10.9 nm for Nd-TiO<sub>2</sub>. For pristine TiO<sub>2</sub>, the crystallite size was 18.8 nm. It has been noted that crystallite size decreases with increasing surface area. Literature reports [26,27,35,36] have demonstrated that, because of the larger radii of rare earth ions, they did not enter into the TiO<sub>2</sub> crystal lattice to substitute for Ti<sup>4+</sup> but rather are distributed on the surface of TiO<sub>2</sub> forming the bond RE–O–Ti. Furthermore, RE–O–Ti bonds around TiO<sub>2</sub> particles could inhibit the growth of crystal grains, thus reducing the specific surface area [37].

# 3.3. Scanning electron microscopy

Scanning electron microscopy was used to characterize the morphology of the obtained photocatalysts. Fig. 3 shows an SEM image of pristine TiO<sub>2</sub> and Nd-modified TiO<sub>2</sub>, and it is observed that aggregation occurred in all samples. Pristine TiO<sub>2</sub> particles were found to be in the larger form of aggregates, unlike Ndmodified TiO<sub>2</sub>. Neodymium ion modification preferably retarded the aggregation and growth of well-dispersed particles. Correlation between the extent of segregation with dosage of neodymium was not observed. Moreover, particles of Nd-TiO<sub>2</sub> were found to be spherical in shape with a diameter in the range of  $0.3-1 \mu m$ , and the SEM-EDX analysis of the 0.25% Nd-modified TiO<sub>2</sub> sample revealed the presence and uniform distribution of neodymium in the synthesized photocatalyst (Fig. 4). Furthermore, the SEM-EDX was applied to determine the elements of samples. The average elements content was calculated based on EDX analysis from the area  $1 \times 1 \mu m$  of each sample. The EDX analysis revealed the presence of titanium, oxygen, carbon and neodymium atoms in the compositions of prepared samples (Table S1). Further information



Fig. 3. SEM images of TiO<sub>2</sub> and Nd-TiO<sub>2</sub>.



Fig. 4. SEM-EDX image of 0.25% Nd-TiO<sub>2</sub>.

about the composition of the surface photocatalysts was provided by the XPS method.

#### 3.4. X-ray photoelectron spectroscopy (XPS)

The elemental contents and chemical character of elements in the surface layer of pristine and Nd-modified TiO<sub>2</sub> samples were examined by XPS. The high-resolution (HR) XPS spectra of Ti2p, O1s, C1s and Nd 4d were recorded for detected elements; titanium, oxygen, carbon and neodymium, respectively. The deconvoluted spectra are presented in Fig. 5 and the XPS data are summarized in Table 2. The presence of neodymium was confirmed all modified samples (see Nd 4d spectra in Fig. 5). The contents of neodymium (in wt.%) agree well with a nominal amount of Nd used during all samples preparation (Table 1). Deconvoluted Ti 2p, O 1s and C 1s core level spectra reveal a chemical character of titanium, oxygen and carbon species, respectively (Fig. 5 and Table 2). Two chemical states of titanium were separated in the Ti 2p spectrum at the BE of Ti  $2p_{3/2}$  peak close to 458.4 eV and 456.8 eV, which can be identified as Ti<sup>4+</sup> and Ti<sup>3+</sup>, respectively. The small amount of reduced titanium (Ti<sup>3+</sup>) is usually observed in all titania samples due to oxygen

defects in the titania lattice. It was reported that even faceted anatase photocatalysts of high crystallinity and uniform morphology, e.g., octahedral and decahedral anatase particles, contained a small amount of Ti<sup>3+</sup> [38,39]. The highest Ti<sup>3+</sup> content was observed for the 0.25% Nd-TiO<sub>2</sub> sample (5.56%). The oxygen peak can be deconvoluted into three peaks, where the most intense one at 529.7 eV indicates the presence of oxygen in the titania lattice (TiO<sub>2</sub>) [40,41]. Two other peaks at 530.2 eV and 531.2 eV can be related to Ti–O surface species (Ti-(OH)-Ti, TiOx) and –C=O, –OH groups, respectively. It is known that the surface modification of titania usually results in a decrease in the intensity of the last peaks because modifiers replace the hydroxyl groups [28,39]. Consequently, an increase in the content of oxygen in the form of TiO<sub>2</sub> correlates with a decrease in the O/Ti ratio. In the present study, a similar observation was noted for some Nd-TiO<sub>2</sub> samples (a decrease of O/Ti and an increase of Ti-O<sub>latt</sub> contribution (Table 2)). Therefore, it is proposed that a small number of neodymium ions formed a surface complex as described in Fig. 6. The formation of the complex between the f orbital of Nd with oxygen increases the photocatalytic activity, providing an effective environment for better interactions among the organic contaminants and hydro-



Fig. 5. XPS spectra of pristine TiO<sub>2</sub> and Nd-TiO<sub>2</sub>.

xyl radicals [42]. Deconvolution of the carbon peak results in three peaks at BE 284.6, 286 and 288.7 eV due to the presence of carbon in the form of C—C, C—OH and C=O, respectively. Usually, carbon originates from the atmosphere and is always detected in all titania samples. Moreover, the precursor of titania (titanium isopropoxide) can be a source of carbon in the sample. A decrease in the carbon content with an increase in neodymium content (Table 2) may suggest the replacement of carbon on the titania surface with neodymium.

#### 3.5. Photoluminescence spectroscopy

Photoluminescence properties of prepared samples are presented in Fig. 7a. Under excitation by light at  $\lambda_{ex}$  = 315 nm, powders showed a weak broad emission band with a maximum intensity at around 350–700 nm with four bands. The first band at approximately 420 nm was attributed to the TiO<sub>2</sub> octahedral, and the observed emissions at 440, 480 and 524 nm were associated with recombination of charge carriers. The maximum of the emission band depends on the type of recombination taking place and could shift in the whole spectral range [43]. It can be seen that unmodified and Nd-TiO<sub>2</sub> nanoparticles can exhibit obvious excitonic PL signals with a similar curve shape, demonstrating that Nd<sup>3+</sup> modification does not give rise to new PL phenomena and emission from Nd<sup>3+</sup> ions is minimal in the presented range, which is consistent with the literature and relates to the spectroscopic properties of Nd<sup>3+</sup> ions [18,27,32]. This is due to spectroscopic properties of rare earth ions, resulting from electron transitions within the 4f subshell and shielding properties of 5s and 5p outer orbitals. Upon analyzing the spectrum, it may be noted that the neodymium-modified TiO<sub>2</sub> caused a decrease in intensity compared to that of pristine TiO<sub>2</sub>. This indicates that Nd<sup>3+</sup> effectively inhibits the recombination of electron-hole pairs. In addition, it can be seen that a small dose of Nd<sup>3+</sup> can reduce the photoluminescence intensity, which suggests that the appropriate amount doping significantly inhibited the recombination of the photogenerated charge carriers. Photoluminescent properties follows the order 0.1 < 0.25 < 1.0 < 0.5 < 0 mol% Nd<sup>3+</sup>. When the amount of neodymium is 0.1 mol%, the intensity reaches a minimum value, indicating that the 0.1 mol% Nd-TiO<sub>2</sub> has the highest separation efficiency of electrons and holes. Based on available literature, it can be concluded that the effect of rare earth ions on photoluminescence properties of TiO<sub>2</sub> is ambiguous. Xiao et al. [32] observed a decrease in intensity of PL with an increase in the content of samarium  $(0.5 < 1.0 < 1.5 < 0 \text{ mol}\% \text{ Sm}^{3+})$ , whereas according to research by Liqiang et al. [27], PL properties changed in the order 0 < 5.0 < 0.5 < 3.0 < 1.0 mol% La<sup>3+</sup>

Photoluminescence spectra recorded in the wider range and with the excitation wavelength  $\lambda_{ex} = 350$  nm (Fig. 7b) showed an intense emission peak with a maximum at approximately 880 nm. The observed emission relates to the  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$  electronic transition of Nd<sup>3+</sup> ions. Furthermore, less intense emission peaks were observed below 850 nm, resulting from the presence of Nd<sup>3+</sup> ions in the structure of the material. The emission of

		Ti fraction (%)			O fraction (%)				C fractior.	1 (%)			Atomic	
		concentration ratio												
Sample	Σ Ti (wt.%)	Ti(4+)	Ti(3+)	Σ0	Ti-O <sub>latt</sub>	Ti-O <sub>surf</sub>	−C=0, −OH 531.4 ± 0.2 eV	Σ C (wt.%)	U-U	с—он,	—C=0,	∑ Nd (wt.%)	C/Ti	0/Ti
		458.4 ± 0.2 eV	456.8 ± 0.2 eV	(wt.%)	529.7 ± 0.2 eV	530.6±0.2 eV			284.6 eV	286.0±0.1 eV	288.7 ± 0.1 eV			
TiO <sub>2</sub>	51.19	94.93	5.07	44.01	78.31	16.77	4.92	4.80	62.89	29.59	4.52	0	0.37	2.57
0.1%Nd-TiO <sub>2</sub>	50.80	95.25	4.75	43.46	80.25	14.00	5.75	5.65	69.34	19.01	11.65	0.09	0.44	2.56
0.25%Nd-TiO <sub>2</sub>	51.77	94.44	5.56	43.87	75.89	18.96	5.15	4.10	65.92	27.54	6.54	0.26	0.32	2.54
0.5%Nd-TiO <sub>2</sub>	53.53	97.42	2.58	44.82	79.76	16.66	3.58	1.16	68.76	8.12	23.12	0.48	.000	2.51
1.0%Nd-TiO <sub>2</sub>	52.56	96.40	3.60	44.43	82.58	13.69	3.73	1.97	70.81	13.11	16.08	1.05	0.15	2.53



Fig. 6. Surface complex formation between Nd and TiO<sub>2</sub>.

Nd<sup>3+</sup> ions is much more intense than that of TiO<sub>2</sub> as a result of the recombination mechanism (band with maximum intensity at around 350–700 nm, see Fig. 7a). This is the reason for the direct excitation of Nd<sup>3+</sup> ions at 350 nm (through to  ${}^{4}I_{9/2} \rightarrow {}^{5}D_{1/2}$ ,  ${}^{2}I_{11/2}$ ,  ${}^{5}D_{5/2}$ , and  ${}^{5}D_{3/2}$  transitions) into their higher excited states [44], which was not observed with  $\lambda_{ex}$  = 315 nm (Fig. 7a). Furthermore, the spectral behaviour of Nd<sup>3+</sup> is different from that of TiO<sub>2</sub> due to the spectroscopic properties of rare earth ions. The characteristic narrow emission bands result from the electron transitions within the 4f subshell and shielding properties of 5s and 5p outer orbitals.

By taking into consideration Nd<sup>3+</sup>-dependent photoluminescence of TiO<sub>2</sub>, we can also assume energy transfer from the TiO<sub>2</sub> host compound to Nd<sup>3+</sup> ions, which could explain the quenching effect of Nd<sup>3+</sup> ions on the TiO<sub>2</sub> photoluminescence. Nd<sup>3+</sup> ions are prone to cross-relaxation (energy migration between Nd<sup>3+</sup> ions); therefore, samples with a concentration of Nd<sup>3+</sup> ions above 0.25% showed a decrease in luminescence intensity [45]. This process is also responsible for the ratio between observed Nd<sup>3+</sup> transition bands from which  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$  is less sensitive for cross-relaxation than others. Furthermore, the relatively low doping level in which cross-relaxation becomes visible suggests the presence of Nd<sup>3+</sup> clusters in the material or the existence of the Nd<sub>2</sub>O<sub>3</sub> phase.

Unfortunately, up-conversion of  $Nd^{3+}$  ions was not detected under excitation wavelengths in the Vis-NIR range. The phenomenon of  $Nd^{3+}$  up-conversion is possible only in low phonon host compounds such as fluorides or chlorides [46]. In oxides, the mechanism of up-conversion is affected by properties of crystal structure and multiphonon relaxation processes [46,47]. Additionally, the TiO<sub>2</sub> host compound may absorb the energy from the Nd<sup>3+</sup> ions excited by NIR photons.

# 3.6. Photocatalytic activity of Nd-TiO<sub>2</sub>

The photocatalytic properties of Nd-TiO<sub>2</sub> NPs were investigated by observing the decomposition of phenol in an aqueous solution under UV–Vis ( $\lambda$  > 350 nm) and Vis ( $\lambda$  > 420 nm) light. Pristine TiO<sub>2</sub> and P25 were used as reference samples. The results of phenol photodegradation after 60 min of exposure to irradiation are shown in Table 3 and Fig. 8. The highest UV-Vis activity was observed for TiO<sub>2</sub> modified with 0.5 mol% of Nd<sup>3+</sup> with the efficiency of phenol degradation reaching 38.54% after 60 min of irradiation. However, all Nd-modified TiO<sub>2</sub> is less active under UV-Vis light in comparison to that of P25. This phenomenon could be explained by the spectroscopic properties of RE<sup>3+</sup> ions. RE<sup>3+</sup> absorbed UV irradiation and emitted energy in the conversion process of luminescence, lowered the excitation of TiO<sub>2</sub> [28]. Fig. 8b shows the visible light photoactivity, which exhibits a decreasing trend with an increasing dosage of neodymium  $(0.1 > 0.25 > 0.5 > 1.0 \text{ mol}\% \text{ Nd}^{3+})$ . The photocatalysts 0.1 mol% Nd-modified TiO<sub>2</sub> exhibited the highest photocatalytic activity. The efficiency of phenol decomposition measured after 60 min of irradiation was 28.03%. It was found that all Nd-TiO<sub>2</sub> revealed higher photocatalytic activity than those of P25 and pristine TiO<sub>2</sub> under visible light irradiation. The probably reason for the low photocatalytic activity of the pristine sample results from the fact that Nd<sup>3+</sup> ions, acting as a Lewis acid, could act as an effective elec-



Fig. 7. (a) Photoluminescence spectra under UV light ( $\lambda_{ex}$  = 315 nm) of Nd-TiO<sub>2</sub> photocatalysts compared to that of pristine TiO<sub>2</sub>. (b) Up-conversion spectra of the TiO<sub>2</sub> samples modified with Nd<sup>3+</sup> under excitation of a laser at  $\lambda_{ex}$  = 350 nm.

Table 3	
Efficiency of phenol degradation under UV-Vis and Vis irradiation and intermediate product formation under Vis light in the presence of Nd-TiO <sub>2</sub> .	

Sample label	Phenol degradation after 60 min UV–Vis (λ > 350 nm) irradiation (%)	Phenol degradation after 60 min of Vis (λ > 420 nm) irradiation (%)	Amount of phenol after 60 min of Vis irradiation (mg/L)	Amount of intermediate products after 60 min of Vis irradiation (mg/L)		
				Benzoquinone	Hydroquinone	Catechol
TiO <sub>2</sub>	24.48	4.74	19.05	Below detection	ı limit	
0.1%Nd-TiO <sub>2</sub>	28.84	28.03	14.39	0.54	1.28	0.74
0.25%Nd-TiO <sub>2</sub>	34.48	22.47	15.51	0.51	1.00	0.70
0.5%Nd-TiO <sub>2</sub>	38.54	22.09	15.58	0.50	1.01	0.65
1.0%Nd-TiO <sub>2</sub>	34.09	9.45	18.11	0.09	0.22	0.21
P25	94.08	6.60	18.68	-	-	-



Fig. 8. Photoactivity under (a) UV–Vis ( $\lambda$  > 350 nm) and (b) Vis ( $\lambda$  > 420 nm) light of Nd-TiO<sub>2</sub> photocatalysts compared to those of pristine TiO<sub>2</sub> and P25.

tron scavenger to trap the conduction band electron of TiO<sub>2</sub> [34]. Xiao et al. [32] and Reszczyńska et al. [48] in their study also observed a decrease in photocatalytic activity under Vis irradiation, increasing the amount of  $RE^{3+}$  (0.5 > 1.0 > 1.5 > 0 mol%  $Sm^{3+}$  and 0.25 > 0.5 > 0 > 1.0 mol%  $Er^{3+}$ , respectively). Lower photoactivity could be explained by blocking of the TiO<sub>2</sub> surface by Nd<sup>3+</sup> ions as well as to an increase in recombination of charge carriers. There

was no correlation between surface area and photoactivity. Which suggests that there is an optimum doping content of  $Nd^{3+}$  ions in TiO<sub>2</sub> particles. Some studies showed that the larger BET surface area of RE-TiO<sub>2</sub> photocatalysts would be beneficial to achieve better adsorption of reagents in aqueous suspension. However, it was noticeable that a larger specific surface area of RE-TiO<sub>2</sub> with a higher RE ions dosage did not lead to a higher photocatalytic activ-

ity, which might be limited by lower separation efficiency of charge carriers [32].

### 3.7. Detection of reactive species

To identify the possible mechanisms of photocatalytic degradation of phenol, especially to understand what type of oxygen species are generated under ultraviolet and visible light photocatalysis, tests with terephthalic acid (TPA) were performed. Terephthalic acid can produce fluorescent compounds (2hydroxyterephthalic acid) by reaction with hydroxyl radicals [49]. Thus, the intensity of the fluorescent band is proportional to the amount of 'OH radicals produced in water. Pristine TiO<sub>2</sub> and blank sample (terephthalic acid) were taken as reference samples. Fig. 9a shows the fluorescence spectra intensity change observed after 60 min of irradiation of Nd-TiO<sub>2</sub> under UV-Vis light. A series of photocatalysts modified by neodymium has shown that the introduction of Nd<sup>3+</sup> increases the intensity of the bands compared to that of an unmodified sample. This indicates that Nd<sup>3+</sup> effectively leads to an increase in the production of 'OH radicals on the surface of the photocatalysts under UV-Vis light irradiation. The obtained results show a correlation between the effectiveness of the generated hydroxyl radicals exhibited and photocatalytic activity under UV-Vis light. The intensity of the fluorescence spectra varied as  $0.1 < 0.25 < 1.0 < 0.5 \text{ mol}\% \text{ Nd}^{3+}$ , which responds to photocatalytic activity. Published literature demonstrates that degradation of pollutants in the UV/TiO<sub>2</sub> system occurs by oxidation of the chemical compounds by hydroxyl radicals [50]. Hydroxyl radicals attack the phenyl ring, leading to catechol and hydroquinone as new intermediate products of degradation. Then, the phenyl rings in these compounds are broken to give shortchain organic compounds, such as formic acid, acetic acid and finally carbon dioxide [51]. Fig. 9b shows the fluorescence spectra intensity change observed after 60 min of irradiation of Nd- modified TiO<sub>2</sub> under Vis light. Fluorescence spectra of pristine TiO<sub>2</sub> and Nd-TiO<sub>2</sub> exhibited nearly the same intensity and this intensity is very low compared with literature data [10]. The intensity of the bands was much lower (approximately 20 times) than under UV-Vis irradiation. This suggests that Nd-TiO<sub>2</sub> modification does not lead to an increase in the production of 'OH radicals under Vis irradiation. Most likely, the photodegradation process occurs as a direct transfer of charge carriers from the photocatalyst to the contaminant and subsequent radical reactions [51,52]. The obtained results show that the photocatalytic activity under Vis irradiation is attributable to other forms of reactive oxygen species such as  $O_2$ ,  $H_2O_2$ , and OOH [12]. To confirm the role of generated of the reactive oxygen species in the photocatalytic process, the photocatalytic activity test in the water phase was conducted in the presence of 0.1%Nd-TiO<sub>2</sub> and scavenger. Silver nitrate, ammonium oxalate, benzoquinone and tert-butanol were used as scavengers of e<sup>-</sup>, h<sup>+</sup>, O<sub>2</sub><sup>-</sup> and OH radicals, respectively. The results of phenol photodegradation presence of scavenger after 60 min of exposure to Vis irradiation are shown in Fig. 10a. The phenol degradation in the presence of silver nitrate and benzoquinone caused a negligible decrease in the photocatalytic efficiency (approximately 3.75 and 5%, respectively). While the photocatalytic efficiency of phenol degradation in the presence of ammonium oxalate and tert-butanol reached 23.87 and 25.02%, respectively. These results confirm the crucial role of  $e^-$  and  $O_2^$ in the photocatalytic degradation of phenol under Vis irradiation. Results of HPLC analysis showed (Table 3) that the main intermediate product detected after 60 min of irradiation under visible light was hydroquinone. Other identified intermediate products included were catechol and benzoguinone. Based on the most active sample (0.1%Nd-TiO<sub>2</sub>), it was observed that the concentration of products in the aqueous phase increased through 60 min of irradiation (Fig. 10b). The degradation is slow with no selectivity among the organic compounds, which are gradually decomposed over time with exposure to Vis irradiation which means that different by-products were produced and degraded at the same time. Determination of Total Organic Carbon showed the beginning of mineralization but at a very low level (results not shown).

#### 4. Discussion of the mechanism

The up-conversion process involves excitation of a material with lower energy photons, which stimulates emission of higher energy photons [53]. According to energy-level diagrams (Fig. 11a) showing the neodymium excitation under visible irradiation, the up-conversion process can be achieved through a series of processes such as ground state absorption (GSA) and excited state absorption (ESA) [28,54]. To explain the possible mechanism of neodymium-modified titania photocatalyst excitation under visible light, the photodegradation of phenol was investigated as a function of irradiation wavelength. Based on quantum efficiency measurements as a function of the excitation wavelength (action spectra), it is possible to determine which aspect of light absorbed by the photocatalyst is involved in photocatalytic reactions. The



Fig. 9. Fluorescence spectral changes in solution of terephthalic acid under (a) UV–Vis ( $\lambda$  > 350 nm) and (b) Vis ( $\lambda$  > 420 nm) light irradiation.



**Fig. 10.** (a) Photocatalytic decomposition of phenol in the presence of 0.1%Nd-TiO<sub>2</sub> and scavenger after 60 min of visible ( $\lambda > 420$  nm) irradiation. (b) Efficiency of phenol degradation and intermediate product formation under visible light ( $\lambda > 420$  nm) in the presence of 0.1%Nd-TiO<sub>2</sub>.



**Fig. 11.** (a) Simplified energy-level diagrams and excitation path for the up-conversion of emission at ultraviolet light Nd<sup>3+</sup> under visible light excitation ( $\lambda$  = 578 nm); GSA, ground state absorption; ESA, excited state absorption. (b) Action spectrum of phenol oxidation on neodymium-modified TiO<sub>2</sub> (Apparent quantum efficiency – squares and circles) and absorption spectrum (K-M function – lines).

results for the sample 0.25% Nd-TiO<sub>2</sub> and pristine TiO<sub>2</sub> are shown in Fig. 11b. The sample modified with 0.25 mol% was selected for the analysis because it show the most intense emission band in the visible light region (Fig. 7b). Action spectra of samples did not resemble the respective absorption spectra (K-M function). Photocatalytic activity under visible light is from irradiation ranging from 400 to 480 nm. There is no activity observed for wavelengths ( $\lambda$  = 525, 585, 745, and 805 nm) characteristic of the presence of neodymium. These wavelengths should be responsible for the up-conversion process. Based on the obtained measurements (luminescence spectra and action spectra), it can be concluded that the conversion process of visible to ultraviolet irradiation does not have a significant effect on the photocatalytic activity of the photocatalysts obtained. The up-conversion process is thus likely not responsible for the degradation of phenol under Vis irradiation. This may be due to the distance between the ground and excited states of neodymium ions and affected by properties of crystal structure and multiphonon relaxation processes [46,47]. Different results have been obtained by Castañeda-Contreras et al. [22], who reported that the process of transforming visible to ultraviolet light by erbium ions is responsible for methylene blue photodegradation under 532 nm laser beam

light. Reszczyńska et al. suggested that differences in the results obtained (no up-conversion process of  $RE^{3+}$ -TiO<sub>2</sub>) could be related to the use of different radiation power sources power: xenon lamp and laser [28,29].

Based on the obtained results, it could be suggested that neodymium ions can form complexes between the f-orbital of Nd with oxygen and are also present as Nd<sup>3+</sup> clusters and in the form of oxides on the TiO<sub>2</sub> surface. The concentration of the organic pollutant at the photocatalyst could provide a mechanism for the enhanced degradation by Nd-modified TiO<sub>2</sub>. Moreover, Nd-modified TiO<sub>2</sub> may result in the formation of oxygen vacancies and surface defects. This process can greatly suppress the recombination and promotion of the separation of electrons and holes pairs, contributing to the enhanced photooxidation ability of holes, while the electrons are easier to react with oxygen molecules to generate another reactive oxygen species for degradation of the pollutant.

# 5. Conclusions

A hydrothermal method was used for the preparation of Ndmodified TiO<sub>2</sub> nanoparticles. SEM-EDX analysis revealed the presence and uniform distribution of neodymium in the synthesized photocatalyst. XPS and PL analysis revealed that neodymium was present in the form of a complex with oxygen, Nd<sup>3+</sup> clusters and oxides on the TiO<sub>2</sub> surface. The prepared samples can achieve photocatalytic degradation of phenol under visible light ( $\lambda > 420$  nm), and Nd-TiO<sub>2</sub> has better activity than those of pristine TiO<sub>2</sub> and P25. Action spectra analysis showed that Nd-modified TiO<sub>2</sub> could be excited under visible light in the range of 400–480 nm. Based on the luminescence and action spectra, it can be concluded that the conversion process of the visible to ultraviolet irradiation does not have a significant effect on the photocatalytic activity of the photocatalysts obtained. The up-conversion process is likely not responsible for the degradation of phenol under Vis irradiation. The enhanced activity is related to increase in the adsorption sites, BET surface area, decrease of the crystallite size and prevention of electron–hole recombination.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2017.07.017.

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