



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



Patrycja Parnicka<sup>a</sup>, Paweł Mazierski<sup>a</sup>, Tomasz Grzyb<sup>b</sup>, Zhishun Wei<sup>c</sup>, Ewa Kowalska<sup>c</sup>, Bunsho Ohtani<sup>c</sup>, Wojciech Lisowski<sup>d</sup>, Tomasz Klimczuk<sup>e</sup>, Joanna Nadolna<sup>a,\*</sup>

<sup>a</sup> Department of Environmental Technology, University of Gdansk, 80-308 Gdansk, Poland

<sup>b</sup> Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University in Poznan, 60-780 Poznan, Poland

<sup>c</sup> Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan

<sup>d</sup> Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

<sup>e</sup> Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, 80-233 Gdansk, Poland

## ARTICLE INFO

### Article history:

Received 5 June 2017

Revised 18 July 2017

Accepted 19 July 2017

Available online 7 August 2017

### Keywords:

Heterogeneous photocatalysis

TiO<sub>2</sub>

Modified-TiO<sub>2</sub>

Rare earth metal

Neodymium

Visible light photoactivity

Phenol degradation

Action spectra analysis

## 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 m<sup>2</sup>/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<sup>-</sup> and O<sub>2</sub><sup>•-</sup> 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].

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<sup>3+</sup>, Ce<sup>3+</sup>, Ce<sup>4+</sup>, Eu<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup> and La<sup>3+</sup>) [17]. Bokare et al. used Nd-TiO<sub>2</sub> materials, synthesized

\* Corresponding author.

E-mail address: [joanna.nadolna@ug.edu.pl](mailto:joanna.nadolna@ug.edu.pl) (J. Nadolna).

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 Nd-modified 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<sub>2</sub>, 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 μS) 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 <sub>BET</sub> (m <sup>2</sup> /g)	Crystallite size (nm)
TiO <sub>2</sub>	None	107	18.8
0.1%Nd-TiO <sub>2</sub>	0.1	124	10.9
0.25%Nd-TiO <sub>2</sub>	0.25	141	8.8
0.5%Nd-TiO <sub>2</sub>	0.5	146	6.8
1.0%Nd-TiO <sub>2</sub>	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<sub>4</sub> 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 Kα radiation (40 kV tube voltage and 20 mA tube current). Measurements were performed in a 2θ 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 X-ray photoelectron spectroscopy (XPS) on a PHI 5000 VersaProbe™ (ULVAC-PHI) spectrometer with monochromatic Al Kα radiation (hν = 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

Download English Version:

<https://daneshyari.com/en/article/6455586>

Download Persian Version:

<https://daneshyari.com/article/6455586>

[Daneshyari.com](https://daneshyari.com)