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Žerjav, G., Say, Z., Zavašnik, J. et al (2023). Photo, thermal and photothermal activity of TiO₂ supported Pt catalysts for plasmon-driven environmental applications. *Journal of Environmental Chemical Engineering*, 11(3). <http://dx.doi.org/10.1016/j.jece.2023.110209>

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Photo, thermal and photothermal activity of TiO₂ supported Pt catalysts for plasmon-driven environmental applications

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ARTICLE INFO

Editor: Javier Marugan

Keywords:

Heterogeneous photocatalysis

TiO₂

Plasmonic noble metal

Pt particles

Visible-light illumination

Schottky barrier height

Bisphenol A

Wastewater treatment

NO_x abatement

Air cleaning

Microreactor

Thermal catalysis

Photothermal catalysis

H₂-deNO_x

ABSTRACT

TiO₂+Pt plasmonic solids with 1 wt% Pt and different TiO₂ supports (anatase nanoparticles (TNP), polycrystalline nanorods (a-TNR) and single-crystal anatase nanorods (TNR)) were synthesized using the wet impregnation technique and tested as photo, thermal and photothermal catalysts in gas-solid and gas-liquid-solid reactions. Due to the different charges of the TiO₂ support surfaces, Pt particles with different sizes, crystallinities and degrees of interaction with the TiO₂ supports were formed during the synthesis. The heights of the Schottky barrier (SBH) were 0.38 eV for the a-TNR+Pt, 0.41 eV for the TNP+Pt, and 0.50 eV for the TNR+Pt samples, respectively. The low visible-light-triggered photocatalytic activity of the TNR+Pt catalyst toward the oxidation of water-dissolved bisphenol A (BPA) is attributed to its high SBH and active site deactivation due to the adsorption of BPA and/or BPA oxidation products. The highest photothermal catalytic H₂-assisted NO₂ reduction rate was expressed by the TNR+Pt catalyst. This can be ascribed to the presence of a narrow particle size distribution of small Pt particles, the absence of the Pt catalysed reduction of the TNR support at higher temperatures, and the lower rate of re-injection of "hot electrons" from the TNR support to the Pt particles.

1. Introduction

The socio-economic development in the past decades has increased organic wastewater pollution with a huge impact on human health [1, 2]. Wastewater treatment technologies can be classified into physical (sedimentation, adsorption, membrane separation), biological (activated sludge and biofilm) and chemical treatment methods [3–6]. The advantage of the chemical treatment methods is that they can rapidly oxidize and completely degrade the organic pollutants without producing secondary waste products [7]. Advanced oxidation processes (AOPs), including Fenton oxidation, photocatalytic oxidation, catalytic wet air oxidation (CWAO), etc., especially exhibit high oxidation reaction rates, high mineralization efficiency, and a low level of secondary pollutant production [8–10]. Through the generation of highly active

reactive oxygen species (ROS, hydroxyl radicals (•OH), superoxide radicals (O₂⁻), etc.), the AOPs can fully degrade organic pollutants into CO₂ and H₂O in the final process called mineralization. Among the AOPs, photocatalytic oxidation technology is especially considered an energy-saving green technology to treat organically polluted wastewater as only a photocatalyst and illumination with light are required, with no need for the addition of chemical agents, such as ozone. Photocatalysts, most commonly semiconductors, are used that upon illumination with light, the energy of which is the same or higher than the band gap energy of the catalyst, produce electrons (*e*⁻) and holes (*h*⁺). The generated charge carriers are further used to directly degrade water-dissolved organic pollutants or to produce ROS. The generated charge carriers can also be recombined to produce heat, but then they cannot be used for the degradation of organic pollutants in wastewater.

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<https://doi.org/10.1016/j.jece.2023.110209>

Received 18 April 2023; Received in revised form 23 May 2023; Accepted 25 May 2023

Available online 26 May 2023

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Two factors determine the quantum efficiency of a photocatalytic material. The first is the electron-hole pair recombination rate and the second is the light utilization efficiency. The quantum efficiency of the most commonly used and investigated photocatalyst in heterogeneous photocatalysis, titanium dioxide (TiO₂), suffers from its two major drawbacks, namely a high electron-hole recombination rate and a high band gap energy (3.0–3.4 eV) [11]. Due to this, only UV-light illumination can be employed to trigger TiO₂ to generate charge carriers, which makes the photocatalytic process cost-ineffective. Different approaches/methods can be used to improve the quantum efficiency, for example, (i) forming a heterojunction with another semiconductor [12–14], (ii) elemental doping [15], (iii) morphology control [16], (iv) the deposition of noble plasmonic metals (PM; Au, Ag, Pd, Pt) [17,18], etc. The deposition of a noble metal onto TiO₂ enables the generation of charge carriers under visible-light illumination due to the localized surface plasmon resonance (LSPR) effect expressed by the PM [19]. Further, an electronic potential barrier, the so-called Schottky barrier (SB), is formed at the noble metal-semiconductor heterojunction, which inhibits the recombination of the visible-light-generated charge carriers and promotes the interfacial charge transfer [20]. Žerjav et al. [18] reported that the selection of the TiO₂ support could significantly influence the properties of the TiO₂ +PM photocatalysts and their photocatalytic activity.

Furthermore, the anthropogenic activities in recent decades have not only influenced the quality of aquatic bodies but also led to high emissions of nitrogen oxides (NO_x) into the atmosphere, which can significantly impact animal and human health and vegetation [21]. Due to the presence of NO_x, especially NO and NO₂, various environmental problems can be created, such as the formation of acid rain, photochemical smog, greenhouse effect etc. NO_x present in the atmosphere can further react with other air pollutants (volatile organic compounds (VOC)) and form products (for example, peroxyacyl nitrate (PAN), nitrous acid, etc.) that are even more harmful to humans than NO_x [22]. The NO_x removal methods can be divided into primary and secondary procedures [23]. The primary NO_x removal methods are carried out inside a combustion zone (for example, a furnace) without the need for another reactor and the NO_x reduction is maintained/directed by the adjustment of the combustion parameters. The most commonly used secondary NO_x removal methods are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) [24,25]. The SCR is realized by introducing different reducing agents (e.g. H₂, CO, NH₃, HC, etc.) and usually occurs on the catalyst surface at between 300 and 400 °C. The disadvantages of using HC and NH₃ in SCR are poor low-temperature activity and the deterioration of the catalysts [26–28]. The advantage of using H₂ as a reducing agent is that it can reduce NO_x at relatively low temperatures and produces low emissions of greenhouse gasses [29,30]. In the past, researchers demonstrated [31,32] that supported Pt catalysts exhibited activity toward the H₂-assisted NO_x-SCR, although the deNO_x activity at low temperatures (<200 °C) should be improved [33]. The improvement of the low-temperature deNO_x activity of catalysts can be, for instance, achieved by the use of a photothermal catalytic process, which is a hybrid technology where the advantages of thermal and photo-based catalytic approaches are synergistically combined [34–36]. The materials used as a catalyst in photothermal catalysis should function as a photo and as a thermal catalyst. It was reported that TiO₂ +Pt-based materials displayed activity under hybrid photothermal conditions as both photo and thermal catalysts [37].

The aim of the present study was to investigate in detail how the optical, electronic and catalytic properties of TiO₂ +Pt catalysts with 1 wt% Pt loading depend on the textural and morphological properties of the TiO₂ support. For this purpose, we used three different TiO₂ supports, i.e. anatase nanoparticles (TNP), polycrystalline nanorods (a-TNR) and single-crystal anatase nanorods (TNR). Special attention in this work was given to the use of the X-ray photoelectron spectroscopy (XPS) technique to determine the height of SB (SBH) in the investigated materials and to correlate it with the photocatalytic activity of TiO₂ +Pt

catalysts. Furthermore, the aim was also to investigate the multifunctional use of the prepared catalysts by using the same material as a photo, thermal and photothermal catalyst in various environmental cleaning applications. The ability of the synthesized TiO₂ +Pt materials to be used as a photocatalyst for the wastewater treatment was tested in a batch slurry reactor under visible-light illumination using water-dissolved bisphenol A (BPA) as a model organic pollutant. In addition, the prepared solids were examined in a catalytic model reaction to evaluate the activity during NO_x reduction in the presence of H₂ as a reducing agent, conceptually demonstrating an alternative approach for low-temperature NO_x abatement that was further enhanced/upgraded by photocatalysis where visible-light illumination was employed.

2. Experimental

2.1. Catalyst synthesis

Three different TiO₂ supports were used in a wet-impregnation synthesis procedure to prepare TiO₂ +Pt catalysts. At first, we used the commercially available TiO₂ support DT-51 (donated by CristalAC-TRiV™, France), which is denoted as TNP (TiO₂ nanoparticles). TNP was also used in a hydrothermal procedure [14] to prepare the second TiO₂ support, polycrystalline TiO₂ nanorods (denoted as a-TNR). The third TiO₂ support prepared in this study was a-TNR calcined at 500 °C for 2 h so that the polycrystalline TiO₂ nanorods transformed into single-crystal anatase TiO₂ nanorods (denoted as TNR). To obtain TiO₂ +Pt catalysts with 1 wt% of Pt loading, 1 g of TiO₂ support was added to a diamminedinitroplatinum(II) (Pt(NH₃)₂(NO₂)₂) aqueous solution (50 ml) and stirred for 20 h. After drying overnight at 60 °C, the samples were calcined at 450 °C for 3 h (heat ramp 10 °C/min). The prepared TiO₂ +Pt catalysts were denoted as TNP+Pt, a-TNR+Pt and TNR+Pt.

2.2. SEM, N₂ physisorption, XRD, zeta potential, H₂-TPD and Pt dispersion analyses

The morphology and chemical composition of the synthesised TiO₂ +Pt catalysts were analysed using a field-emission scanning electron microscope (FE-SEM, SUPRA 35 VP, Carl Zeiss) equipped with an energy-dispersive X-ray spectrometer (EDS, model Inca 400, Oxford Instruments). Further, the crystal structure and phase composition were assessed using a transmission electron microscope (TEM, JEM-2100, JEOL) operating at 200 keV. The micrographs were recorded by a high-resolution slow-scan CCD camera (Orius SC1000, Gatan Inc.).

The N₂ adsorption/desorption isotherms of the materials were obtained at –196 °C with the use of Micromeritics' TriStar II 3020 analyser. Prior to the measurements, the samples were pre-treated in Micromeritics' SmartPrep degasser in a stream of N₂ (Linde, purity 6.0) for 60 min at 90 °C and further for 240 min at 180 °C.

The phase composition of the prepared catalysts was measured using an X-ray powder diffraction diffractometer (XRD, X'pert PRO MPD, PANalytical) utilising Cu Kα₁ radiation (λ = 1.54056 Å) in reflection geometry between 10 and 90° and steps of 0.0341°. The results were interpreted using a PDF database from the International Centre for Diffraction Data (ICDD).

A Malvern Panalytical Ultra Red zetasizer equipped with an automatic titration device was used to determine the zeta potential of the investigated bare TiO₂ supports in the pH range from 2 to 9 using HCl and NaOH solutions to control the pH value. Before the measurements, 25 mg of the investigated TiO₂ supports were dispersed for 30 min in 100 ml of distilled water using an IKA Lab Disc ultra-flat stirrer.

An AutoChem II 2920 apparatus from Micromeritics, fitted with a Thermal Conductivity Detector (TCD), was employed to perform temperature-programmed reduction analysis (H₂-TPR) of the prepared catalysts. During the measurement, 100 mg of the sample was positioned on a quartz wool flock inside a U-shaped quartz tube and pre-treated in 5% O₂/He at 350 °C for 10 min, followed by cooling to –50 °C. After 5

min, the flow was changed to 5% H₂/Ar and a linear temperature ramp of 10 °C/min was employed until the final temperature of 550 °C was reached.

CO chemisorption analysis was performed using a Micromeritics AutoChem II 2920 instrument. The catalyst samples were weighed (150 mg each) and placed on a quartz wool flock plugged in a U-shaped quartz tube. The catalyst was reduced by 5% H₂/Ar at 400 °C for 30 min. After reduction, the sample was purged with pure He for 30 min and cooled down to 35 °C at 10 °C/min. Once the baseline was stable, CO chemisorption was performed, where 0.53 ml (STP) of 5% CO/He was injected into the He stream. The CO gas injection was repeated 30 times. A TCD signal vs. time plot was obtained and the Peak Editor software was used to estimate the area under the peaks in order to calculate the metal dispersion values.

2.3. EIS, UV-Vis DR, XPS and PL analyses

A Metrohm Autolab potentiostat/galvanostat PGSTAT302N equipped with an electrochemical impedance spectroscopy (EIS) FRA32M module was used to perform EIS measurements under Schott KL 1600 LED visible-light illumination in the frequency range of 0.1–10⁶ Hz. To carry out the experiments in 0.1 M KOH electrolyte, a Metrohm DropSens Ramacell PTFE electrochemical cell was employed. The investigated materials were immobilized on the working electrode of the disposable Metrohm DropSens DRP-150 screen-printed carbon electrodes.

A Perkin-Elmer Lambda 35 UV-Vis spectrophotometer equipped with the RSA-PE-19 M Praying Mantis accessory for powdered samples was used to obtain the UV-Vis diffuse reflectance spectra of the prepared materials. The background correction was performed with the Spectralon® material.

The photoluminescence (PL) emission spectra of the prepared catalysts were recorded by means of a Perkin-Elmer LS-55 UV-Vis fluorescence spectrophotometer at the excitation wavelength of 315 nm.

X-Ray Photoelectron Spectroscopy analysis was performed using the Supra+ instrument (XPS, Kratos, Manchester, UK) equipped with an Al K_α excitation source and a monochromator. The powder samples were attached to double-sided tape, and the analyses were performed with an analysed spot size of 300 by 700 μm. The charge neutralizer was on during the analyses. High-resolution and survey spectra were measured with a pass energy of 20 and 160 eV, respectively. Spectra acquisition and data processing were performed using the ESCAPE 1.4 software (Kratos, Manchester, UK).

2.4. Heterogeneous photocatalytic oxidation of an aqueous solution of bisphenol A

The photocatalytic degradation experiments of water-dissolved bisphenol A (Sigma-Aldrich, c₀(BPA)= 10.00 mg/l) under visible-light illumination (Philips 150 W halogen lamp) in the presence of the investigated materials (c_{cat.}=125 mg/l) were carried out at 25 °C and atmospheric pressure in a 250 ml Lenz Laborglas glass batch slurry reactor (model LF60). The bisphenol A/catalyst aqueous suspension was purged with 45 l/h of air and stirred at 600 rpm during the experiment. The so-called “dark” phase (30 min) was introduced before illumination with visible light to establish the sorption process equilibrium of bisphenol A onto the catalyst surface. An HPLC instrument (Thermo Scientific, model Spectra) was employed to monitor the degradation of bisphenol A as a function of the reaction/visible-light illumination time. For this purpose, a 100 × 4.6 mm BDS Hypersil C18 (2.4 μm) column was used and more details about the utilized HPLC analytical protocol can be found in our previous publication [38]. A total organic carbon analyser (Teledyne Tekmar, model Torch) was used to obtain data on the total organic carbon (TOC) content in fresh and treated BPA solutions with an observed measurement error within ± 1% for each of the three repetitions. A Perkin-Elmer 2400 Series II CHNS analyser was further

used to determine the amount of carbon accumulated on the surface of the investigated catalysts during the BPA degradation runs.

2.5. H₂-assisted NO₂ photo and thermal catalytic reduction

The photo and thermal catalytic H₂-assisted NO₂ degradation reactions were conducted in a temperature-controlled Harrick Praying Mantis reaction chamber designed for Raman spectroscopy. The examined catalysts were aimed to be packed as thin as possible (4 mm, 20 mg), so that the maximum absorption of light was ensured. A Pfeiffer Vacuum Omnistar mass spectrometer was connected to the reaction chamber outlet for a quantitative real-time analysis of gaseous products. The catalyst samples were exposed to a gas mixture of 5000 ppm NO₂ and 5% H₂ in Ar with 70 ml/min gas flow. The samples were subsequently pre-treated in pure Ar for 60 min at 350 °C. Then the reactor was cooled down to 30 °C and exposed to the reaction mixture for 1 h for the conditioning and stabilization of the mass spectrometer. After that, the samples were gradually heated from 30° to 400°C with a 12 °C/min heating ramp.

The results from the thermal catalytic NO₂ reduction were further used to determine the temperature range for carrying out the photo-thermal catalytic NO₂ reduction. The catalyst samples were pre-treated in the same way as before in the thermal catalytic NO₂ degradation experiments. The photo-thermal catalytic NO₂ reduction runs were conducted in the temperature range of 50–200 °C with a temperature step of 25 °C. At each temperature step, the catalysts were initially in the dark for 15 min, so that the stabilization of the mass spectrometer response was established. After this, the samples were illuminated with a visible-light source for another 15 min. An OSRAM halogen lamp in 64657 HLX Newport 67011 arc lamp housing with a 69921 power supply, and a 1 m fibreglass light guide were used as a light source for the photocatalytic experiments.

3. Results and discussion

3.1. Characterization of photocatalysts

The size and morphology of the catalysts were assessed by SEM. Particulates in the a-TNR and TNR samples show a rod-like morphology with a diameter of ~10 nm and a length of 80–100 nm. In the TNP sample, we identified ellipsoidal TiO₂ particles with a length of 30 nm and a diameter of 20 nm (Fig. S1). The synthesis procedure of TiO₂ +Pt catalysts did not influence the morphology of the TiO₂ supports; the SEM-EDS chemical composition analysis of powders shows well-dispersed Pt particles (Fig. S2), and the actual loading of Pt is equal to the nominal one (SEM-EDS results are listed in Table S1).

The XRD diffractograms of the investigated materials illustrated in Fig. 1 show peaks that are typical for anatase TiO₂ (JCPDS 00-021-1272). In the XRD diffractogram of the bare a-TNR sample, the intensities of the peaks belonging to the anatase TiO₂ are very low, which can be ascribed to the amorphous TiO₂ shell covering the anatase core. In the XRD diffractograms of TNR and a-TNR+Pt samples, the intensities of anatase peaks are very strong, which provides evidence that the thermal treatment during the synthesis of TNR and a-TNR+Pt solids caused the crystallization of the amorphous TiO₂ shell in the a-TNR support into anatase phase. The average anatase crystallite size was calculated using the Scherrer formula from the width of the (001) diffraction peak (2θ=25°). The results listed in Table 1 show that the average anatase crystallite size in the bare TiO₂ supports is between 10 nm (a-TNR solid) and 19 nm (TNP and TNR samples), and that due to the thermal treatment during the synthesis procedure the anatase crystallite size in a-TNR+Pt catalyst increased to 17.4 nm. In the case of the TNR+Pt and TNP+Pt catalysts, the anatase crystallite size was not influenced by the deposition of Pt particles. The low intensity or absence of Pt diffraction peaks in the acquired XRD diffractograms of TiO₂ +Pt catalysts (Fig. 2) can be ascribed to the low amount of deposited Pt,

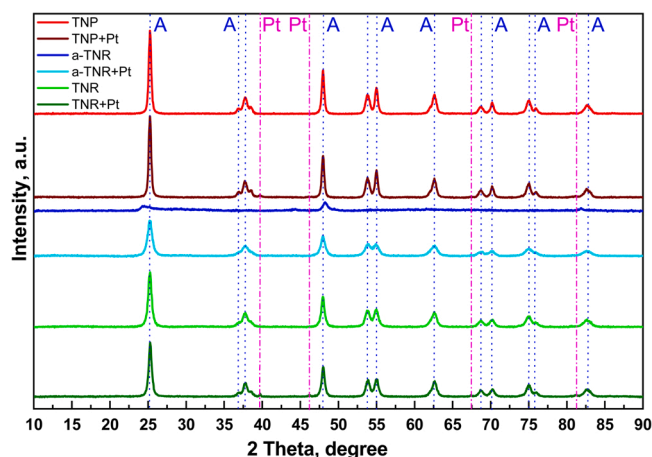


Fig. 1. XRD patterns of bare TiO₂ supports and synthesized TiO₂ +Pt catalysts. The vertical lines denote the standard data of anatase (blue, JCPDS no. 71–1167) and Pt (magenta, JCPDS no. 04–0802).

weak crystallinity, non-spherical shape and small size of the Pt particles, and/or the high dispersion of Pt particles over the TiO₂ supports [39–42]. The results of the XRD and TEM-SAED analysis show that in all the investigated samples, TiO₂ is only present in anatase form and that the calcination carried out at 300 and 500 °C did not result in the anatase-to-rutile transformation.

The representative samples were analysed by TEM; the particulates were directly visualized at different magnification scales, while their phase composition was analysed via selective-area electron diffraction (SAED) (Fig. 2). In the case of the TNP sample, the TiO₂ crystallites are near-spherical, with an average crystallite size of 17 nm (Std. dev. 5.5, min 6 nm, max 30 nm). For TNR samples, the TiO₂ particles are anisotropic with a similar diameter (~10–15 nm) while their length differs: a-TNR particles are shorter (~20 nm) while TNR particles appear longer (~100 nm). Although on the micron level, both TNR samples appear to have similar dimensions, we measured the size of the crystallites here and not only the size of the particles.

The TEM-selected area electron diffraction (SAED) patterns of the prepared TiO₂ +Pt catalysts (inset in Fig. 2, with ab-initio simulations for anatase, Pt, and their mixture) correspond to anatase TiO₂ and the minor presence of Pt in all the examined TiO₂ +Pt samples. The crystallite size of the Pt particles in the catalysts was measured from the TEM micrographs (Fig. 2) and the results are listed in Table 1. The particle size distribution of Pt particles in the TiO₂ +Pt catalysts in Fig. S3 show that the size of the Pt particles depends on the TiO₂ support employed. The size of Pt crystallites in TNR+Pt solid is ~2–3 nm, while for the TNP+Pt and a-TNR samples, the Pt crystallites appear larger and ~5–7 nm.

As shown by Žerjav et al. [18], the size of PM particles in the TiO₂ +PM catalysts can be influenced by the difference in the zeta potential value (pH_{PZC}) of TiO₂ supports. In this regard, we measured the zeta

potential of the bare TiO₂ supports and the pH value of the aqueous Pt(NH₃)₂(NO₂)₂ solution used for the deposition of Pt particles. From the results presented in Fig. S4, we can see that the investigated TiO₂ supports can be divided into two groups based on the pH_{PZC} values. The pH_{PZC} values of the TNP and a-TNR samples are 2.8 and 3.5, and that of the TNR support equals 7.2, which means that the surfaces of the TNP and a-TNR supports are deprotonated during the wet impregnation procedure, and that of TNR support is protonated, because the pH value of the aqueous Pt(NH₃)₂(NO₂)₂ solution is 5.0. The negative charge of the TNP and a-TNR surfaces during the wet impregnation procedure positively influences the adsorption of the Pt(NH₃)₂²⁺ complex [43,44] through a strong electrostatic attraction, compared to the positive charge of the TNR surface, and consequently larger Pt particles are formed in the case of TNP+Pt and a-TNR+Pt samples. We should further emphasize that the particle size distribution in the case of TNR+Pt catalyst was narrower than in the case of TNP and a-TNR supports (Fig. S3). In the case of TNP+Pt catalyst especially, a widespread Pt particle size distribution can be observed with smaller (below 2 nm) and larger (above 8 nm) Pt particles.

The diversity in the morphology of TiO₂ supports was also well expressed in the results of the N₂ physisorption analysis listed in Table 1. The corresponding N₂ adsorption-desorption isotherms and BJH pore size distributions are illustrated in Fig. S5. The specific surface areas (S_{BET}) of the bare TiO₂ supports are between 85.8 m²/g (TNP) and 352 m²/g (a-TNR). From our previous publications, we know that the a-TNR sample exhibits a core-shell structure consisting of an amorphous TiO₂ shell and anatase TiO₂ core, where upon the thermal treatment, the amorphous TiO₂ shell crystallizes into anatase TiO₂ [14]. The S_{BET} and pore volume (V_{pore}) values of the TNR and a-TNR+Pt samples decreased and the values of the pore diameter (d_{pore}) increased in comparison to the values of the a-TNR sample due to the crystallization of the amorphous TiO₂ shell, which leads to the elimination of micropores contained in the amorphous TiO₂ shell. The S_{BET}, V_{pore} and d_{pore} values of the TNP+Pt and TNR+Pt catalysts did not change significantly in comparison to the pure TiO₂ supports, which implies that the deposited Pt particles did not block the pores of the TiO₂ supports.

Fig. 3 presents the UV-Vis diffuse reflectance (UV-Vis DR) spectra and the corresponding Kubelka-Munk function of bare TiO₂ supports and prepared TiO₂ +Pt catalysts. The UV-Vis DR spectra of all the materials show a strong absorption in the wavelength range below 400 nm, which is given by the band gap of TiO₂ [17]. As can be seen in the UV-Vis DR spectra of the investigated TiO₂ +Pt catalysts, the introduction of Pt resulted in an increase of the absorption of light in the region between 400 and 800 nm, which is due to the plasmonic properties of the noble metal and the localized surface plasmon resonance (LSPR) [45]. The band gap values of the investigated solids obtained through the use of the Kubelka-Munk function are listed in Table 1. The absorption edge shift and the energy band change in the TiO₂ +Pt catalysts were only minor in comparison to the bare TiO₂ supports; this suggests that Pt is only deposited on the surface of the TiO₂ supports [42].

Another parameter that significantly influences the photocatalytic activity of a photocatalyst is the recombination rate of the light-

Table 1

Comparison of the specific surface area (S_{BET}), average pore diameter (d_{pore}), total pore volume (V_{pore}), anatase TiO₂ crystallite size at 25 °, band gap values of the investigated materials obtained with the Kubelka-Munk function, Schottky barrier height (SBH), charge transfer resistance (R_{CT}) and the dispersion of Pt particles.

Sample	S _{BET} m ² /g	V _{pore} cm ³ /g	d _{pore} nm	^a TiO ₂ crystallite size @ 25 °	Band gap eV	^b SBH	R _{CT}	Pt dispersion %
TNP	85.8	0.29	13.7	19.0	3.30	/	kΩ	/
TNP+Pt	63.6	0.26	15.7	19.0	3.20	0.41	9.8	13
a-TNR	352	0.96	8.9	10.4	3.40	/	399	/
a-TNR+Pt	149.1	0.63	16.9	17.4	3.25	0.38	17.4	25
TNR	105.0	0.57	19.3	19.0	3.30	/	309	/
TNR+Pt	85.1	0.44	20.0	19.0	3.25	0.50	30.9	26

^a Calculated using the Scherrer formula and assuming that the TiO₂ particles are spherical.

^b Calculated from the determined values of VBM in Fig. 6.

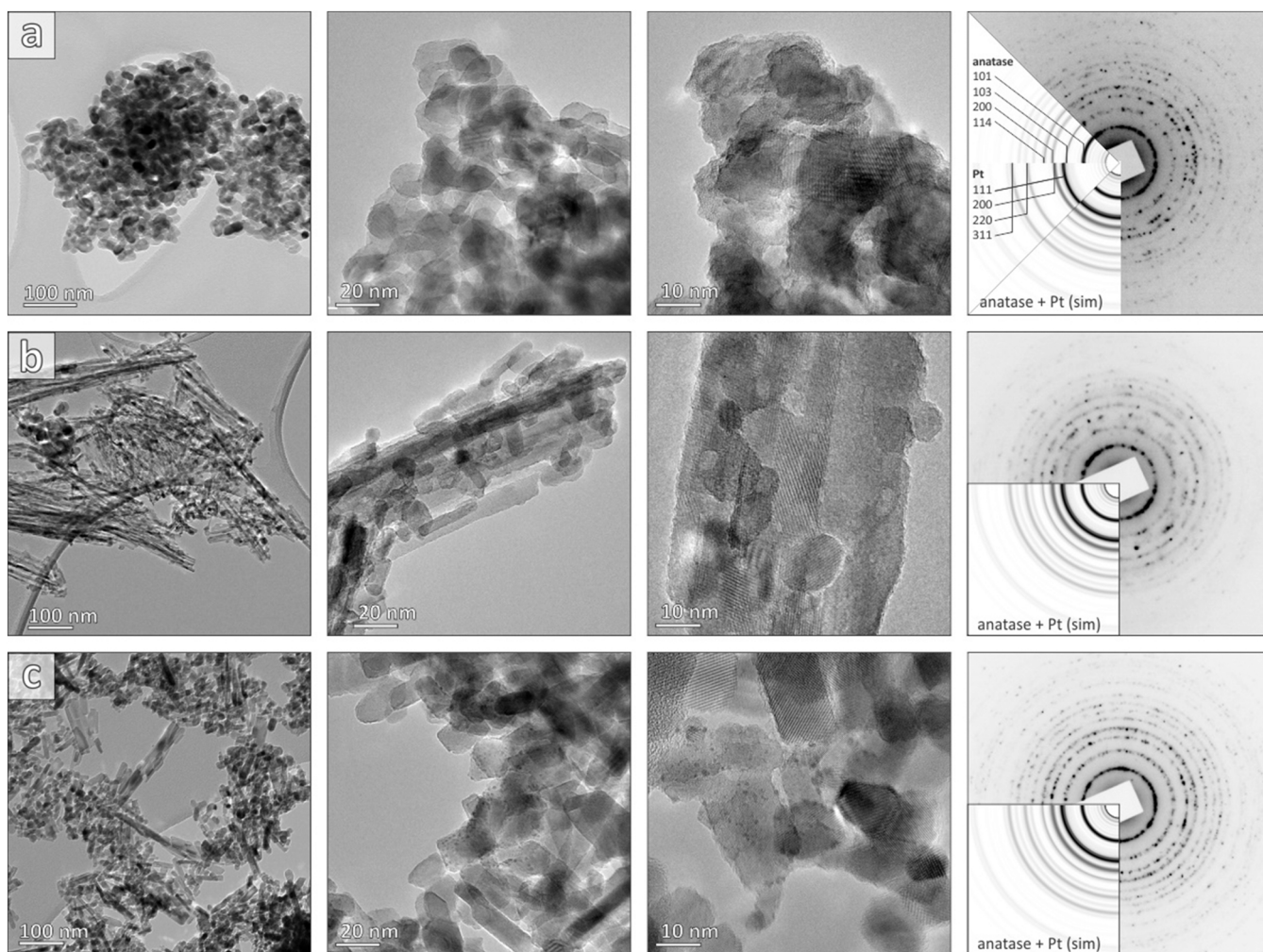


Fig. 2. TEM micrographs of the investigated $\text{TiO}_2 + \text{Pt}$ catalysts obtained at different magnifications and TEM experimental selected area electron diffraction (SAED) patterns of prepared $\text{TiO}_2 + \text{Pt}$ catalysts with simulated patterns of anatase TiO_2 and Pt (a) TNP+Pt, (b) a-TNR+Pt, and (c) TNR+Pt samples).

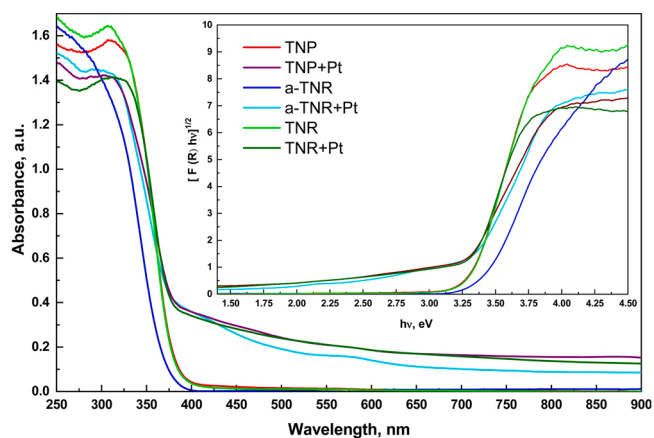


Fig. 3. UV-Vis-DR spectra of the bare TiO_2 supports and synthesized $\text{TiO}_2 + \text{Pt}$ catalysts. The respective Kubelka-Munk function is present in the inset.

generated charge carriers, as a low charge carrier recombination rate is associated with high photocatalytic activity [45,46]. The photo-induced electrons and holes tend to recombine if they don't participate in any ROS generation reaction. With the recombination of charge carriers, energy in the form of photoluminescence (PL) emission is released; therefore, the intensity of the photoluminescence signal of a solid

material is proportional to the electron-hole recombination rate. In the PL spectra of all the investigated materials displayed in Fig. 4, well-resolved shoulders/peaks were observed at around 3.2, 2.93, 2.7, 2.54 and 2.33 eV. Abazović et al. [47] ascribed the well-defined peak at 2.9 eV to the lowest indirect transition $\Gamma_{1b} \rightarrow X_{1a}$ and the signals at around 3.1 eV and above to direct ($X_{1b} \rightarrow X_{2b}$ at 3.59 eV and $X_{1b} \rightarrow X_{1a}$ at

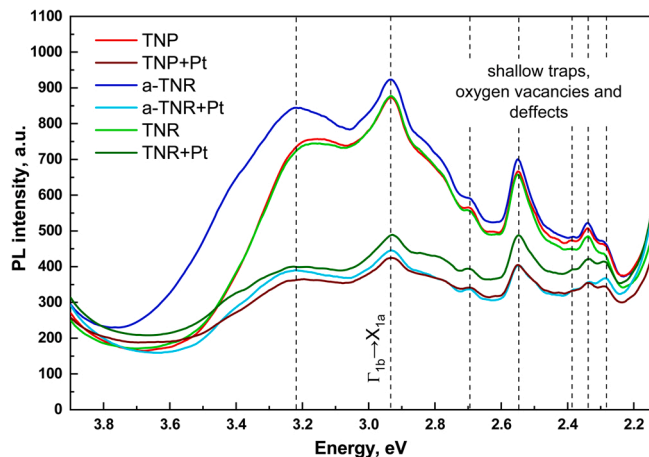


Fig. 4. Solid-state photoluminescence (PL) emission spectra of bare TiO_2 supports and synthesized $\text{TiO}_2 + \text{Pt}$ catalysts.

3.45 eV) and indirect ($X_{1b} \rightarrow \Gamma_3$ at 3.19 eV and $\Gamma_{1b} \rightarrow X_{2b}$ at 3.05 eV) transitions in the anatase TiO_2 . The peaks at 2.8, 2.7, 2.55 and 2.34 eV were further ascribed to the presence of the shallow traps. Kernazhitsky et al. [48], in their study of anatase and rutile TiO_2 solids, ascribed the strong excitonic peak at 2.91 eV to the recombination of self-trapped excitons, the peaks in the range between 2.71 and 2.80 eV to the excitonic recombination of charge carriers via oxygen vacancies, and the peaks at around 3.0 eV to indirect and direct transitions originating from the band-to-band charge carrier recombination. The origin of the decreased PL intensity in the case of the sample TNR, in comparison to the PL intensity of a-TNR solid (Fig. 4), lies in the calcination of the TNR sample at 500 °C and the growth of the anatase crystallite size from 10.4 to 19.0 nm (Fig. 2, Table 1) as the PL processes in solids are strongly affected by particle size, surface and bulk defects, calcination temperature, etc. This phenomenon was also observed by Liqiang et al. [49], who reported that the excitonic PL intensity of TiO_2 decreased due to the calcination of TiO_2 as a consequence of the particle size increase. The enhancement of the PL signal intensity in the PL solid-state spectra of different anatase TiO_2 samples was also observed by Kernazhitsky et al. [50] and attributed to the increase of the specific surface area and the associated increase of surface defect states, oxygen vacancies and the surface hydration degree of the investigated anatase TiO_2 samples. The PL solid-state spectra of the investigated TiO_2 +Pt catalysts in Fig. 4 exhibited lower PL signal intensities in comparison to the solid-state spectra of the bare TiO_2 supports regardless of the TiO_2 support employed. Nakajima et al. [51] attributed the decrease of the PL bands intensity of TiO_2 +Pt catalysts, in comparison to the PL band intensity of the pure TiO_2 supports, to differences in the work function between Pt and TiO_2 and not to differences in the specific surface area of the investigated materials. With the introduction of Pt particles onto the surface of TiO_2 supports, a junction is formed between the TiO_2 and Pt particles, which in turn enables the transport of light-generated “hot electrons” from Pt particles to the TiO_2 support. The role of the TiO_2 support in TiO_2 +Pt catalysts under visible-light illumination is to act as the sink for “hot electrons”, thus prolonging the “lifetime” of the generated charge carriers. This is expressed as the decrease of the PL signal intensities in the PL solid-state spectra of the TiO_2 +Pt solids that can be observed in Fig. 4.

The electrochemical impedance spectroscopy (EIS) measurements were further employed to test the ability of the investigated photocatalysts in terms of the separation of visible-light-generated charge carriers. The electrochemical equivalent circuit (EEC) presented in Fig. S6 and composed of solution resistance (R_s), charge transfer resistance (R_{CT}), Warburg impedance (W), and the constant phase element (CPE), was used to fit the obtained Nyquist plots that are illustrated in Fig. 5. The R_{CT} values in the EEC are listed in Table 1 and indicate the charge transfer resistance at the electrode (photocatalyst)/electrolyte interface, with the diameter of the Nyquist’s plot semicircle that reflects the charge transfer process [52]. The higher charge transfer resistance of a catalyst is expressed as the larger diameter of the semicircle [53–56]. It is not surprising that TiO_2 supports exhibit the highest R_{CT} values (between 138 and 399 k Ω) among the investigated materials. The highest R_{CT} value was obtained in the case of a-TNR sample, which also exhibited the highest BG value and the highest PL signal intensity (Fig. 4). The R_{CT} values of the TiO_2 +Pt catalysts were significantly lower than those of the TiO_2 supports and were in the range between 9.8 and 30.9 k Ω . The results of the EIS measurements show that the presence of Pt particles enables the TiO_2 +Pt catalysts to employ visible-light illumination to generate charge carriers, as was already postulated by the results of the UV-Vis DR spectra measurements (Fig. 3). The differences in the R_{CT} values of the TiO_2 supports originate in their different crystallite sizes, band gap energies and specific surface areas. The same can also be postulated for the TiO_2 +Pt catalysts, but here we also have to consider that at the junction between the TiO_2 support and Pt particles, an SB is formed. The height of the SB at the junction between TiO_2 and plasmonic metal can be influenced by the TiO_2 support [18] and the

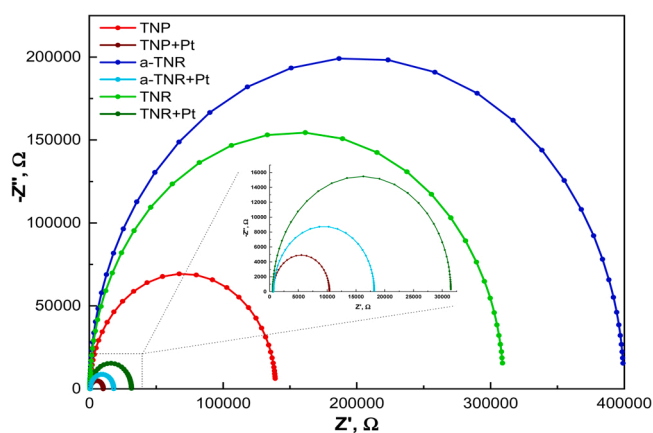


Fig. 5. EIS Nyquist plot of the bare TiO_2 supports and synthesized TiO_2 +Pt catalysts in a 0.1 M KOH electrolyte under visible-light irradiation. The dashed lines represent the data fitted with the electrochemical equivalent circuit presented in Fig. S6.

amount of added PM [17].

The results of the XPS analysis show that the Pt 4f signal was detected for all the TiO_2 +Pt catalysts. The oxidation state of Pt was obtained by fitting the Pt 4f spectra (Fig. S7). The position of the doublets (Pt 4f_{7/2} and Pt 4f_{5/2}) corresponds to the Pt(II) and Pt(0) oxidation states for all three samples (quantitative results are given in Table S2) [57]. The shape and position of the Ti 2p_{3/2} and Ti 2p_{1/2} peaks were similar for all the samples apart from TNR+Pt (Fig. S8a). The latter sample shows a low-intensity shoulder on the high binding energy side, which suggests the presence of Ti(III), whereas the main Ti 2p_{3/2} peak corresponds to Ti(IV). The shape and position of the Ti 2p spectra for all the other samples suggest that the surface is composed of Ti(IV) species [58]. O 1s spectra show three features (Fig. S8b). The feature located at dashed line 1 corresponds to the Ti suboxides and the charge transfer from Ti [59], and was expressed only for the TNR+Pt sample. The main peak for all the samples located at dashed line 2 originates from oxygen in the TiO_2 . The feature at dashed line 3 corresponds to the oxidized carbonaceous species, which adsorbed onto the surface during sample preparation and transfer to the spectrometer [58].

The formation of the Schottky barrier (SB) at the junction between the TiO_2 support and PM particles is expressed by the shift of the valence band maxima (VBM) of the TiO_2 +PM catalysts toward lower binding energies in comparison to the VBM of the bare TiO_2 support [60,61]. Fig. S9 presents a scheme of the band gap diagram of the TiO_2 support/Pt particles system and schematically shows the formation of SBH and the transfer of visible-light-generated “hot electrons” from Pt particles to the TiO_2 support. The net charge transfer occurs continuously until the Fermi levels of both components are aligned [62]. Upon this, an electric field known as SBH (Φ_{SB}) is created at the TiO_2 support/Pt particles junction that results in the presence of a potential barrier for electrons moving from Pt particles to the TiO_2 support and is defined as [63]:

$$\Phi_{SB} = \Phi_M - \chi \quad (1)$$

The Φ_{SB} in Eq. (1) presents the SBH between Pt particles and TiO_2 support, χ represents the electron affinity of TiO_2 , and Φ_M stands for a work function of Pt. The literature search reveals that the electron affinity of TiO_2 is in the range between 4.9 and 5.1 eV [64], and the Φ_M equals to 5.6 eV [65]. The migration of electrons at the TiO_2 /Pt interface is facilitated by lowering of the Φ_{SB} value. The results of the VBM measurements of the investigated materials are illustrated in Fig. 6. The VBM positions of the measured materials with respect to the Fermi level (EF) were found to be 2.91, 3.25 and 2.84 eV for the TNP, a-TNR and TNR samples, respectively. Based on the results of the XPS measurements presented in Fig. 6, the VBM values of the catalysts shifted toward

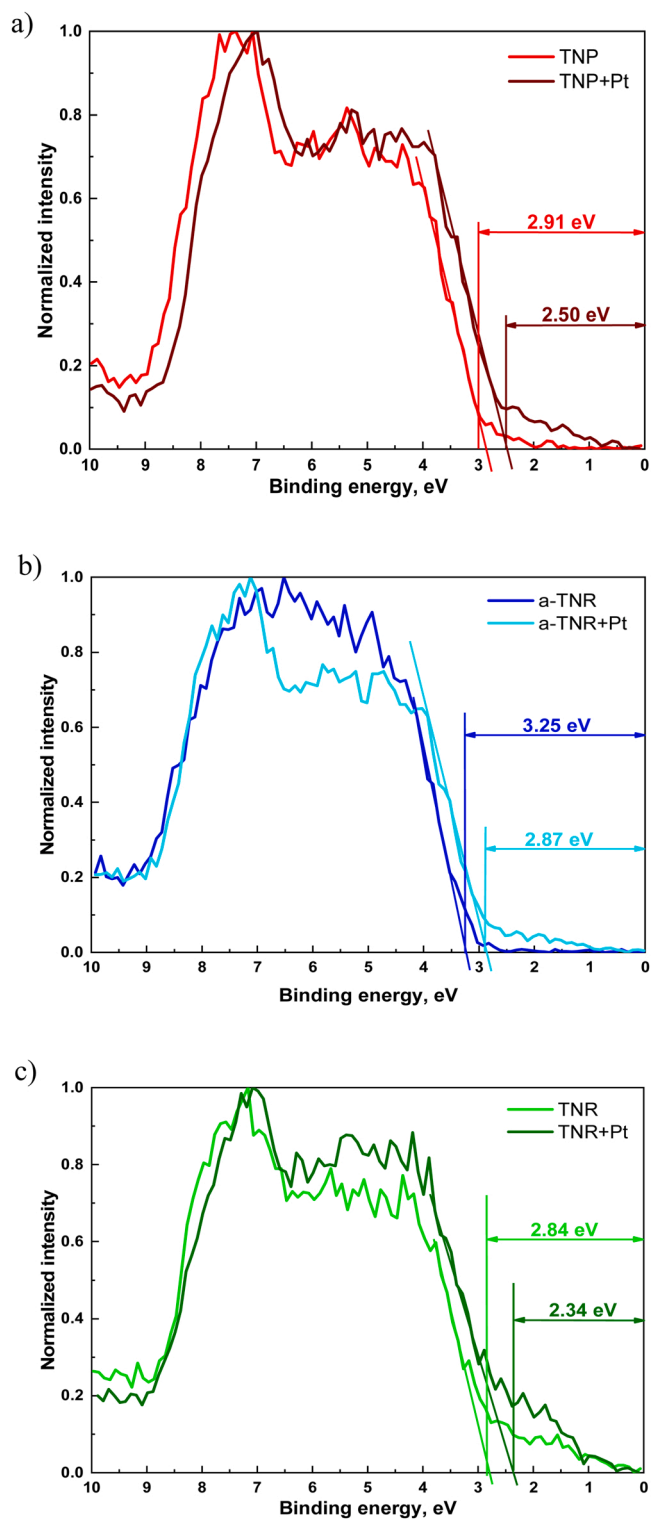


Fig. 6. Determination of the VBM of the bare TiO_2 supports and TiO_2 +Pt catalysts by means of XPS analysis.

lower binding energies in comparison to the VBM values of bare TiO_2 , which means that the ϕ_{SB} values of the investigated a-TNR+Pt, TNR+Pt and TNP+Pt catalysts are 0.38, 0.50 and 0.41 eV, respectively. It was reported previously that the light-generated “hot electrons” in the PM have an energy of 1–2 eV [66–68], which is enough to overcome the SB in all of the investigated TiO_2 +Pt samples. The light-generated “hot electrons” in the TNR+Pt solid need to overcome a higher SB than the

“hot electrons” in the a-TNR+Pt and TNP+Pt catalysts. This means that the “hot electrons” in the TNR+Pt catalyst need more time to overcome the SB. The consequence is that the “hot electrons” agglomerate at the SB and become more susceptible to recombination with the generated Pt holes and so less generated “hot electrons” can be transferred to the TNR support and be used, for example, for ROS generation. This is also in the agreement with the results of the solid-state PL measurements (Fig. 4).

The redox properties of the investigated TiO_2 +Pt samples were analysed by means of the H_2 -TPR technique. Fig. 7 shows the obtained H_2 -TPR profiles of the pre-oxidized TiO_2 +Pt samples. The low-temperature reduction peaks (below 150 °C) can be ascribed to the reduction of Pt oxides to metallic Pt [69–72]. The differences in the position of the low-temperature reduction peaks for the investigated TiO_2 +Pt catalysts can be attributed to differences in the formed Pt oxides (surface platinum oxide (Pt_3O), PtO and PtO_2), as well as differences in the particle size and crystallinity degree of the formed Pt oxides [73,74]. The results of the XPS Pt 4f measurements listed in Table S2 reveal that the different ratios between the Pt(II) and Pt(0) oxidation states occur for the investigated TiO_2 +Pt catalysts. Depending on the TiO_2 support used, different amounts of metallic Pt and Pt oxides are thus formed on the catalyst surface exhibiting different reduction properties. Further, the results of the H_2 -TPR analysis are in accordance with the results of the TEM analysis. In the latter, it was observed that the average particle size of Pt particles depends on the TiO_2 support used and that the smallest Pt particles (average size of ~2–3 nm, Fig. S3) and a narrow Pt particle size distribution were obtained in the case of the TNR+Pt sample. The latter solid exhibited the low-temperature reduction peaks at the lowest temperatures (–10, 30 and 100 °C) among the investigated TiO_2 +Pt catalysts due to the higher reducibility of small Pt particles. The particle size distribution of Pt particles in the case of the TNP+Pt sample (Fig. S3) shows a much broader distribution ranging from small to large Pt particles with an average size of ~5–7 nm. Due to this broadening of the particle size of the Pt particles, the TNP+Pt H_2 -TPR profile exhibits reduction peaks in both the low-temperature range (0–90 °C) and at higher temperatures (350 °C). In the H_2 -TPR profile belonging to the a-TNR+Pt sample, the reduction peak was observed at around 150 °C. The absence of reduction peaks at lower temperatures could be explained by the absence of small diameter Pt particles (below 2 nm), as was shown by the particle size distribution of Pt particles for the a-TNR+Pt sample in Fig. S3. It is well known that a partial reduction of TiO_2 by H_2 occurs at temperatures above 500 °C, therefore, the high-temperature reduction (above 300 °C) observed in the H_2 -TPR profiles of the investigated TiO_2 +Pt samples could be attributed to the Pt-catalysed reduction of TiO_2 (spillover effect) [69, 75]. The literature search revealed that the differences in the

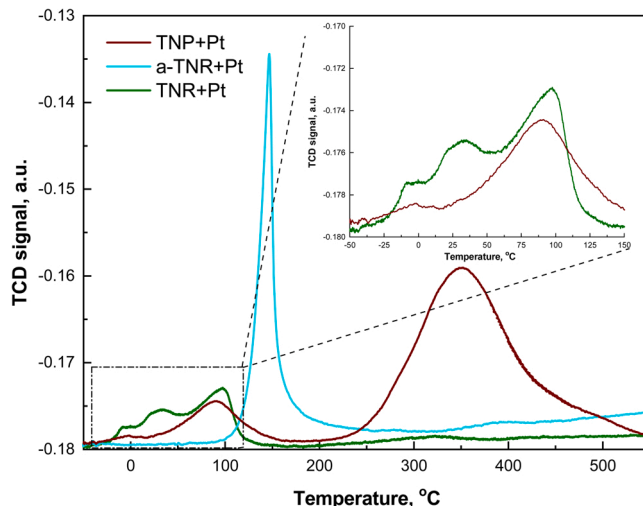


Fig. 7. H_2 -TPR profiles of the investigated TiO_2 +Pt catalysts.

high-temperature H₂-TPR profiles of the examined solids can be ascribed to differences in the interaction of Pt oxides with the TiO₂ supports [76], different dispersion of Pt on the catalyst surface [77], and differences in the specific surface area and crystallinity of the TiO₂ supports [69]. The results of the characterizations performed on the investigated TiO₂ +Pt catalysts revealed that we deal with TiO₂ supports exhibiting different specific surface area and sizes of TiO₂ crystallites (Table 1), as well as different interactions between the TiO₂ supports and Pt particles (Fig. 6, Table 1). Further, the results of the CO chemisorption analysis listed in Table 1 demonstrate that the dispersion of Pt metallic particles depends on the employed TiO₂ support. The above-described differences in the redox properties of the synthesized TiO₂ +Pt catalysts will play a significant role in the H₂-assisted thermal catalytic decomposition of NO_x, as Liu et al. [76] already attributed the improved low-temperature reduction of NO_x carried out over a TiO₂/WO₃ +Pt catalyst in the presence of more reducible Pt oxides, in comparison to the TiO₂ +Pt catalyst. In addition, Nanba et al. [78] showed that the temperature window of the selective reduction of NO with H₂ in the presence of excess O₂ (the NO–H₂–O₂ reaction) over a Pt/Al₂O₃ catalyst is significantly affected by the nature of the Pt particles.

3.2. Catalytic activity

3.2.1. Photocatalytic oxidation of water-dissolved bisphenol A

The ability of the prepared TiO₂ +Pt materials to undergo the visible-light-triggered degradation of water-dissolved bisphenol A (BPA) was tested in a batch slurry reactor system. Preliminary experiments, the results of which are not included in this manuscript, confirmed that the photocatalytic oxidation runs were performed in the kinetic regime and therefore not influenced by mass-transfer resistances. The adsorption of BPA onto the surface of the investigated catalysts was tested during the so-called “dark” period (marked by the grey area in Fig. 8a) of 30 min. The adsorption of BPA onto the surface of bare TiO₂ supports and TiO₂ +Pt catalysts can be neglected, as the results in Fig. 8 show that the BPA concentration in the aqueous solution was constant during the “dark” period for all tested materials.

Pure TiO₂ supports showed a minor BPA degradation under visible-light illumination (between 17% and 25% after 120 min of visible-light irradiation), which was due to the presence of surface Ti³⁺ species or surface defects [79,80]. The addition of Pt onto the TiO₂ supports significantly enhanced the degradation of water-dissolved BPA. The highest photocatalytic activity involving BPA degradation under visible-light illumination was exhibited by the TNP+Pt sample, which showed complete BPA degradation already after 70 min of illumination, followed by the a-TNR+Pt solid that attained complete BPA degradation after 120 min of illumination. The lowest BPA degradation rate was obtained in the presence of the TNR+Pt catalyst, which degraded 80% of the initial BPA amount in 120 min under visible-light illumination.

To monitor the extent of BPA mineralization (i.e. the deep oxidative transformation to CO₂), TOC analysis of fresh and treated BPA solutions, as well as CHNS elemental analysis of fresh and spent catalysts were carried out (Table S3). This enabled us to determine the amount of accumulated BPA and/or BPA degradation products on the surface of the investigated materials (TOC_A). These results were further used to calculate the amount of real mineralization (TOC_M); the data is illustrated in Fig. 8b. One can see that pure TNP, with the lowest specific surface area of all the tested TiO₂ supports, tends to accumulate much less of the BPA degradation products than the bare TNR and a-TNR samples. By introducing Pt particles on the TiO₂ supports, the extent of the mineralization significantly increased. The order of the mineralization extent obtained in the series of TiO₂ +Pt catalysts is the same as the one concerning the BPA degradation rates. The TOC_A values reveal that the higher specific surface area can also have a detrimental effect on the photocatalytic activity of catalysts in heterogeneous photocatalysis for wastewater treatment. Namely, the results in Fig. 8b show that the a-TNR+Pt and TNR+Pt samples exhibit a higher affinity to adsorb BPA

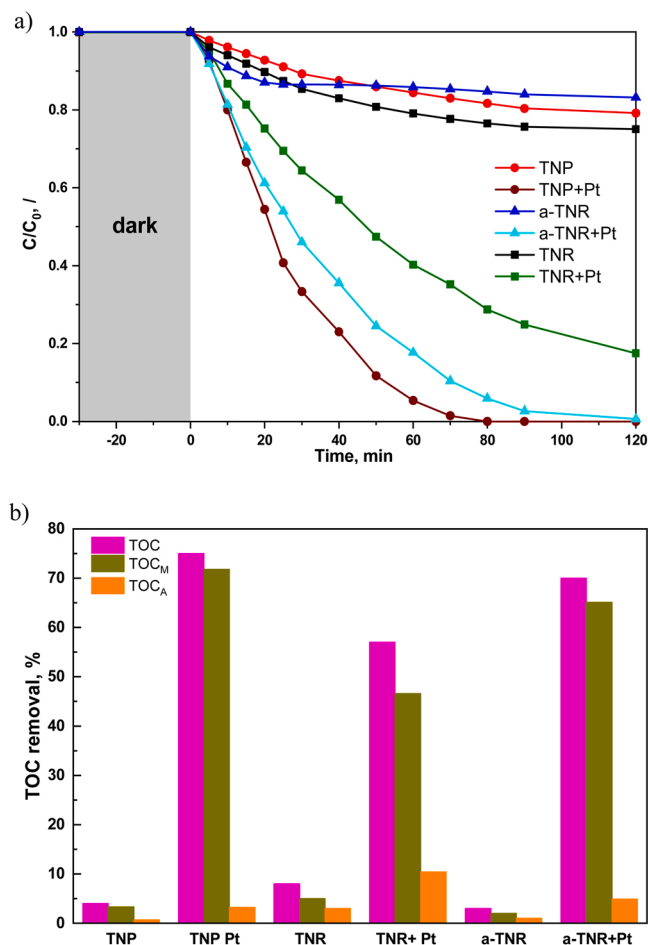


Fig. 8. (a) Photocatalytic degradation of an aqueous solution of BPA ($C_0 = 10.0$ mg/l) conducted at $T = 25$ °C in the presence of bare TiO₂ supports and synthesized TiO₂ +Pt catalysts ($C_{cat.} = 125$ mg/l) under visible-light illumination. (b) The reported values of total organic carbon (TOC) removal represent a sum of TOC mineralization (TOC_M) and TOC accumulation (TOC_A) measured at the end of the BPA degradation runs.

degradation products compared to the TNP+Pt catalyst. Due to this, the surfaces of the a-TNR+Pt and TNR+Pt samples get blocked and cannot participate in the formation of ROS by the generated charge carriers. In the case of a-TNR+Pt sample, the impact of the surface-blocking process on the BPA degradation, expressed at a later stage of the reaction course, is due to the almost 50% higher specific surface area. Another drawback of the TNR+Pt catalyst that decreases photocatalytic efficiency in comparison to the a-TNR+Pt and TNP+Pt samples, is its high SB, which prolongs the transfer time of the generated “hot electrons” into the TNR support and therefore makes them more susceptible to the charge carrier recombination process.

3.2.2. H₂-assisted thermal and photothermal reduction of NO₂

The temperature-dependent direct H₂-assisted NO₂ reduction in the temperature range between 30 and 400 °C was studied over bare TiO₂ supports and TiO₂ +Pt catalysts by monitoring the decrease of the NO₂ concentration (as ion current) in the flow-through (photo)catalytic reactor. The corresponding NO₂ conversions versus temperature dependencies, which are illustrated in Fig. 9a, were calculated based on the calibration curve shown in Fig. S10. In Fig. S11, one can see the results of a blank experiment performed using an empty reactor; they confirm that the reactor walls negligibly contribute to the disappearance of NO₂. The results in Fig. 9a show that bare TiO₂ supports exhibit no catalytic activity toward the degradation of NO₂ in the investigated

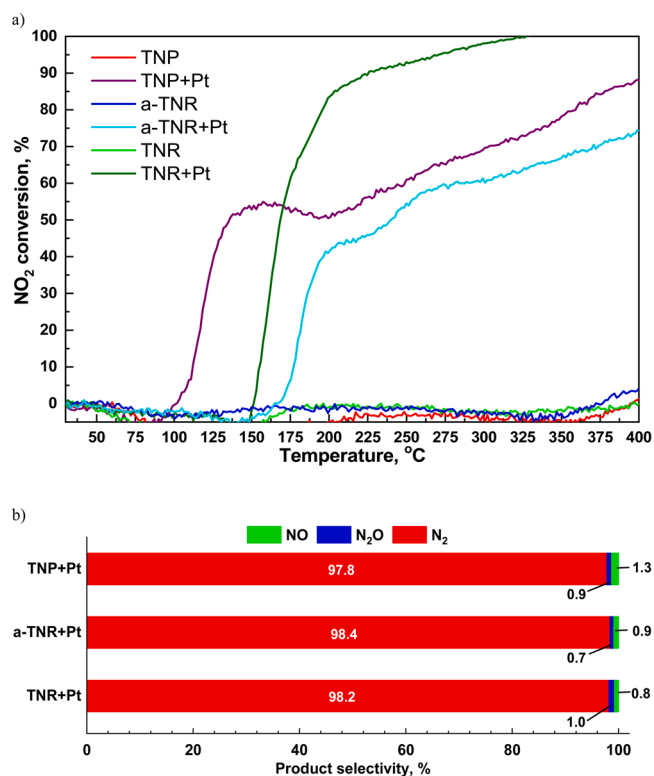


Fig. 9. (a) Temperature-dependent relative NO₂ conversion over bare TiO₂ supports and TiO₂ +Pt catalysts calculated based on the calibration curve present in Fig. S10. (b) Calculated relative percent selectivity of three major products (NO, N₂O and N₂) in the 30–400 °C temperature interval for the investigated TiO₂ +Pt catalysts.

temperature range. The addition of Pt onto TiO₂ supports enables the degradation of NO₂ in the investigated temperature interval, regardless of the employed TiO₂ support, although below 90 °C neither of the investigated TiO₂ +Pt catalysts exhibited any thermal catalytic activity. The lowest activity in the H₂-assisted deNO₂ process in the investigated temperature range was obtained in the presence of the a-TNR+Pt catalyst, while the TNR+Pt sample exhibited the highest activity. Another important aspect to be considered is product selectivity. During the NO₂ reduction using H₂, the three main products are NO, N₂O and N₂. The most desired product is N₂ due to its nontoxic characteristics, while NO and N₂O are major greenhouse and toxic gases. Fig. S12 shows the MS ion current values for the three major detectable products as a function of increasing the reaction temperature from 30° to 400°C. The relative selectivity of the examined catalysts was calculated by integrating the area under ion current curves for each product [81] in the investigated temperature range. The results presented in Fig. 9b are promising, as they reveal that all the examined TiO₂ +Pt catalysts exhibit high selectivity toward N₂ formation (between 97.8% for the TNP+Pt sample and 98.4% for the a-TNR+Pt solid). Although the obtained selectivity values toward N₂ formation among the investigated samples differ only marginally, the difference in the ignition temperature of the H₂-assisted NO₂ reduction process is more significant. The TNP+Pt sample exhibited a reaction ignition temperature of 90 °C, the TNR+Pt sample of 150 °C, and the a-TNR+Pt sample of 159 °C. The differences in the temperature profiles of the NO₂ reduction process obtained by the investigated catalysts can be ascribed to the diversity in the reduction properties of the studied samples, which was observed in the H₂-TPR profiles illustrated in Fig. 7. We can conclude that the presence of easily reducible Pt oxides decreased the ignition temperature of the NO₂ reduction process, as already reported by other authors [76,78]. The decrease and increase of the NO₂ reduction rate exhibited by the

TNP+Pt and a-TNR+Pt samples in the temperature region between 120 and 250 °C (Fig. 9a) can be ascribed to the Pt catalysed reduction of TiO₂.

Further, we investigated if we could lower the ignition temperature of the H₂ deNO₂ process by upgrading the thermal catalysis with photocatalysis. According to the observations of Christopher et al. [82], a decrease of the reaction temperature by 25 °C can increase the lifetime of a catalyst by about ten-fold. The TiO₂ +Pt catalysts were examined in the temperature range between 50 and 200 °C with temperature increments of 25 °C. The samples were first kept at the investigated temperature for 30 min, so that the MS ion current signal was stable. After this, we switched on the light source and waited for another 30 min to obtain a stable MS ion current signal; this was then repeated for each temperature increase. It should be noted that no increase of the temperature due to light illumination was detected by the temperature probe of the reaction chamber. However, we also note that this observation does not rule out a significant temperature increase at the sample position, since the temperature probe of the chamber is located a significant distance from the sample. We can see in Fig. 10 that the light illumination of the catalyst surface increased the extent of NO₂ conversion (here we also used the calibration curve presented in Fig. S10 to calculate the NO₂ conversion values). The highest additional benefit of photocatalysis in the photothermal NO₂ reduction was observed in the presence of the TNR+Pt catalyst. Although this catalyst exhibits the highest SBH, the highest photocatalytic activity of this sample in the NO₂ reduction process among the investigated TiO₂ +Pt catalysts can be ascribed to the second role of the SB at the junction between TiO₂ and PM, which is to prevent “hot electrons” being re-injected from the TiO₂ support to PM particles (Fig. S9). This leads to the accumulation of “hot electrons” in the conduction band of TiO₂, thus enabling them to achieve higher energy levels and increase their reduction potential [83]. In addition, we need to consider that the LSPR effect expressed by Pt particles can also affect the chemical process by heat generation via light absorption and coupling of “hot electrons” to the phonon bath (thermalization) and optical nearfield enhancement [84–86]. The processes can occur separately or side by side, making one of the key efforts in the field of plasmonic catalysis to find out how to distinguish between them [87,88]. Baffou et al. [89] proposed various simple experimental procedures to distinguish between the photothermal process and the “hot carrier” process in plasmonic catalysis, which avoid the use of thermal microscopy techniques. One of them is to plot the measured chemical reaction rate or any readout of the amount of reaction products as a function of the light source power, where a linear dependence under moderate light power and a super-linear dependence for very high light

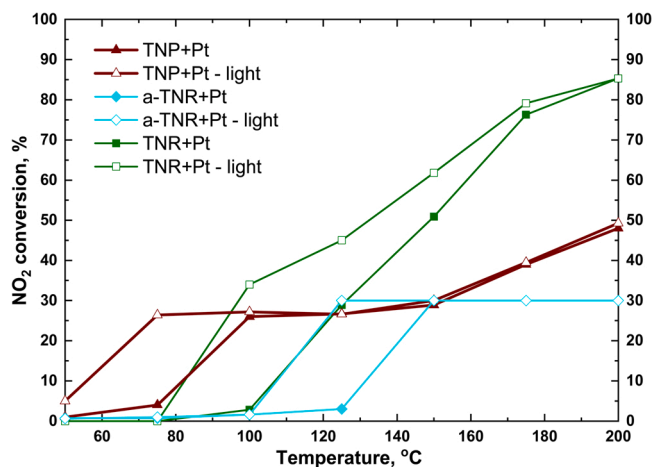


Fig. 10. NO₂ conversion versus temperature curves (solid symbols) and visible-light-assisted NO₂ conversion versus temperature curves (open symbols) over bare TiO₂ supports and TiO₂ +Pt catalysts.

power [90,91] would indicate a photochemical process and an exponential increase a photothermal effect [89]. We performed the photothermal degradation of NO₂ for the investigated samples at the lowest temperatures, at which we observed the highest beneficial influence of photocatalysis (i.e. 75 °C for the TNP+Pt sample, 125 °C for the a-TNR+Pt sample, and 100 °C for the TNR+Pt sample, Fig. 10) dependant on the increasing power of the light source (from 0 to 250 W). Fig. S13 shows the obtained curves of the increase of NO₂ conversion versus illumination light power. In the case of the TNP+Pt and a-TNR+Pt samples, the trends of NO₂ conversion increase follow the linear dependence for moderate light power (dashed blue line in Fig. S13) and super-linear dependence (dashed green line in Fig. S13) for high light power. In the case of the TNR+Pt sample, NO₂ conversion follows the same linear fit regardless of the light power. The obtained experimental data for the a-TNR+Pt and TNR+Pt samples in Fig. S13 also show a good fit if an exponential function is used (dashed red line). The dilemma of whether the same experimental data could be fitted well with linear or exponential functions was also pointed out by Baffou et al. [89]. In practice, it is difficult to obtain an experimental data set that is large enough to be satisfactorily fitted with either exponential or linear functions, as this would mean extremely sensitive measurements of reaction rates at low or very high light powers would be required [89]. We can tentatively conclude that the “nature” of the LSPR effect in the investigated TiO₂ +Pt catalysts differs due to the use of various TiO₂ supports. The purpose of the above discussion was to draw attention to the various influences of the Pt LSPR effect on the chemical process, and to point out that more effort should be devoted to researching this phenomenon in the future. However, the obtained results of the H₂-assisted NO₂ reduction confirm that the investigated TiO₂ +Pt catalysts function as photo and thermal catalysts and can be used as catalysts in hybrid photothermal reaction systems.

Finally, the results of this study reveal that the role of SBH on the catalytic activity of the investigated TiO₂ +Pt photocatalysts depends on the nature of the application used. In the case of the heterogeneous photocatalytic oxidation of aqueous BPA solution, the photocatalytic activity of the investigated TiO₂ +Pt catalysts increases with decreasing SBH, which means that the injection of “hot electrons” into TiO₂ CB has a major impact on the overall photocatalytic BPA degradation efficiency due to the high demand for the “hot electrons” at the TiO₂/liquid interface to participate in the oxygen reduction process to generate ROS (i.e. superoxide anion radicals). Obviously, in the given range of reaction and operating conditions, the concentration of water-dissolved oxygen was sufficiently high not to limit the extent of oxygen surface reduction. On the contrary, in the case of the H₂-assisted deNO_x reduction process, the participation of “hot electrons” in the reduction steps on the TiO₂ surface was not fast, which in turn favoured the re-injection of “hot electrons” from the TiO₂ support to Pt particles. Consequently, a high SBH (like in the TNR+Pt sample) was beneficial to enhance accumulation of “hot electrons” in the TiO₂ CB, allowing them to reach higher energy levels and increasing their reduction potential [83]. However, this remains to be investigated by, for example, conducting the H₂-assisted deNO_x reduction process at higher concentrations of NO₂ in the gas phase.

4. Conclusions

The wet impregnation technique was used to synthesize TiO₂ +Pt catalysts with 1 wt% Pt loading and three different TiO₂ supports, which differ in the specific surface area and the morphology (anatase nanoparticles (TNP, S_{BET}(TNP)= 85 m²/g), polycrystalline nanorods (a-TNR, S_{BET}(a-TNR)= 352 m²/g) and single-crystal anatase nanorods (TNR, S_{BET}(TNR)= 105 m²/g)). The results of TEM and H₂-TPR analyses show that, based on the nature of the TiO₂ support, different average Pt particle sizes and the Pt particle size distribution, species of Pt oxides with different sizes, crystallinities and degrees of interaction with the TiO₂ supports were formed during the wet impregnation procedure. The

negatively charged TNP and a-TNR surfaces strongly attracted the positively charged Pt(NH₃)₂⁺ complex, which resulted in the formation of larger Pt particles (~5–7 nm), in contrast to the positively charged TNR surface where smaller Pt particles (~2–3 nm) were formed. The UV-Vis DR spectra of the investigated solids revealed that the catalysts exhibited the ability to generate charge carriers under visible-light illumination due to the formation of SB, which enabled the separation of charge carriers and the prolongation of their “life” time by transferring the visible-light-generated Pt “hot electrons” to the TiO₂ supports. The SBH in the a-TNR+Pt, TNR+Pt and TNP+Pt samples were obtained by means of XPS analysis and found to be 0.38, 0.50 and 0.41 eV, respectively.

The low-visible-light-triggered photocatalytic activity of the TNR+Pt catalyst involving the oxidation of water-dissolved BPA is attributed to its high SBH and affinity to adsorb BPA and/or BPA degradation products, which means that the generation of ROS during the liquid-phase BPA oxidation process is hindered. The results of the thermal catalytic H₂-assisted NO₂ degradation performed over the TiO₂ +Pt catalysts in the temperature range of 30–400 °C showed that differences in the temperature profiles of the NO₂ reduction process occurred due to the diversity in the reduction properties of the studied solids. The TNP+Pt catalyst exhibited the lowest ignition temperature in the NO₂ reduction due to the presence of easily reducible Pt oxides. In the case of a-TNR+Pt and TNP+Pt catalysts, a decrease in the NO₂ reduction rate was observed in the temperature range of 120–250 °C as a consequence of the Pt catalysed reduction of TiO₂ supports. All the investigated TiO₂ +Pt catalysts exhibited a high selectivity toward N₂ formation of over 97%. In addition, visible-light illumination of TiO₂ +Pt catalysts at temperatures below 200 °C beneficially increased the NO₂ conversion and lowered the ignition temperature of the deNO_x process due to the Pt LSPR effect. The highest catalytic activity involving the H₂-assisted NO₂ reduction observed for the TNR+Pt catalyst can be ascribed to the presence of a narrow particle size distribution of small Pt particles, the absence of the Pt catalysed reduction of the TNR support at higher temperatures, and the beneficial effect of a higher SBH to prevent the re-injection of “hot electrons” from the conduction band of TNR to Pt particles. One should also not forget that the LSPR effect of the Pt particles can affect the NO_x decomposition by the photothermal heat production process.

The results of this study show that the prepared TiO₂ +Pt plasmonic catalysts can be used as photo, thermal and photothermal catalysts in both gas-solid and gas-liquid-solid environmental applications, and that the catalytic performance of the examined solids depends on their morphological, optical and electronic properties, as well as on the properties/conditions of the application in which they are used as catalysts.

CRedit authorship contribution statement

Gregor Žerjav: Conceptualization, Investigation, Validation, Writing – original draft, Visualization, Supervision. **Zafer Say:** Investigation, Writing – review & editing. **Janez Zavašnik:** Investigation, Visualization. **Matjaz Finsgar:** Investigation, Visualization. **Christoph Langhammer:** Writing – review & editing. **Albin Pintar:** Investigation, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

The authors acknowledge the financial support from the Slovenian Research Agency (research core funding nos. P2-0150, P1-0417, P2-0118). The project is co-financed by the Republic of Slovenia, the Ministry of Education, Science and Sport and the European Union under the European Regional Development Fund.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.110209](https://doi.org/10.1016/j.jece.2023.110209).

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