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# Preparation of platinum modified titanium dioxide nanoparticles with the use of laser ablation in water

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We report on the preparation method of nanocrystalline titanium dioxide modified with platinum by using nanosecond laser ablation in liquid (LAL). Titania in the form of anatase crystals has been prepared in a two-stage process. Initially, irradiation by laser beam of titanium metal plate fixed in a glass container filled with deionized water was conducted. After that, ablation process was continued, with the use of platinum target placed in freshly obtained titania colloid. In this work, characterization of obtained nanoparticles, based on spectroscopic techniques: Raman, X-ray photoelectron and UV-vis reflectance spectroscopy is given. High resolution transmission electron microscopy was used to describe particle morphology. On the basis of photocatalytic studies we observed the rate of degradation process of methylene blue (MB) (a model organic pollution) in the presence of Pt modified titania in comparison to pure $TiO_2$ - as a reference case. Physical and chemical mechanism of the formation of platinum modified titania is also discussed here. Stable colloidal suspensions containing Pt modified titanium dioxide crystalline anatase particles show an almost perfect spherical shape with diameters ranging from 5 to 30 nm. The $TiO_2$ nanoparticles decorated with platinum exhibit much higher (up to 30%) photocatalytic activity towards the degradation of MB under UV illumination than pure titania.

## A Introduction

Oxide semiconductors such as $TiO_2$ nanoparticles have been extensively studied for their photocatalytic activities, chemical stability and multiplicity of applications, i.e. in dye sensitized solar cells, water splitting or photodegradation.[1] Most of preparation methods applied to titanium dioxide are based on hydrolysis of organic or inorganic precursors, such as titanium alkoxides[2] or titanium halides[3] followed by calcination processes. The promising alternative for traditional chemical synthesis is laser ablation in liquid.[4] This technique is based on evaporation, of material from metal plate immersed in liquid media using laser beam.[5] In the case when titanium plate is used as a target, the composition of nanoparticles produced by laser ablation strongly depends on the nature of the liquid, i.e. applying dichloroethane as liquid media leads to formation of titanium carbide, while in the presence of ethanol ablation process results in the formation of Ti nanocrystals[6] and, finally, the aquatic environment allows for titania production.[7]

In comparison to classical synthesis methods, laser ablation in liquid allows to obtain nanoparticles without by-products. Futhermore, this method for the synthesis of nanoparticles is simple, quick and straightforward.[8] The particles generated using LAL are stable in water because laser generated particles are charged and thus obtained colloids are not inhalable. That leads to an improved occupational safety for product handling. Additionally, according to literature data,[9] laser produced metal nanoparticles in comparison to chemically obtained particles exhibit higher catalytic activity. It is also worth noting that properties of the nanoparticles, their diameter and narrow distribution can be controlled by adjusting laser radiation parameters, such as energy density, wavelength and pulse duration.[10]

Apart from pure titania, combination of a noble metal (i.e. Pt, Au, Pd) and titanium dioxide regarded as a key semiconductor material has received much attention owing to its wide application in fields ranging from photochemistry to heterogeneous catalysis.[11] Platinum modified titania is most often obtained via chemical synthesis using hexachloroplatinic (IV) acid[12,13] as a platinum source. However, this way of Pt-modified $TiO_2$ production takes a long time (up to a few days[14]), is affected by the temperature of autoclaving or calcinations step and carbon contamination resulting from titania precursor, which cannot be controlled easily. With regard to laser ablation in liquid, we know only the synthesis of Pt-$TiO_2$ in water, based on bi-combinant target: sintered pellet made from $TiO_2$ and Pt mixture, resulting in spindle-shaped particles.[4]

Here we propose an alternative route of pulsed laser ablation in liquid to synthesize platinum modified titania in a water-driven assembly process.[15] This surfactant-free approach is different from stabilizers or other chemical precursor-based preparation methods. The synthesis is based on two-stage ablation process. Initially, a colloid of pure titanium dioxide particles is produced in the ablation process of titanium metal plate immersed in deionized water. In the second stage a Ti target is substituted by a platinum plate and the ablation process is continued. The duration of the second step determines the amount of produced platinum clusters. This study shows that the proposed method constitutes a promising alternative for chemical synthesis of metal oxides like titanium dioxide or zinc oxide modified with noble metal particles, *i.e.* platinum, gold. The performed characterization of obtained particles focused on their morphology, crystalline structure and composition. Furthermore, the photocatalityc activity of prepared colloids towards the degradation of methylene blue as a model organic contaminant was examined. It is shown that Pt modified $TiO_2$ exhibits a higher ability to methylene blue degradation under UV illumination than pure titania.

## B Experimental

A typical experimental setup of pulsed laser ablation in liquid is shown in Fig.1. The experiments were carried out using a Q-switched Nd:YAG (Quantel) pulse laser generating 6 ns pulses at the wavelength of 1064 nm with the repetition rate of 20 Hz. The laser beam was focused with a 100 mm focal length lens on the metal plate immersed in water. The spot size of the laser beam in the plane of metal plate was about 1.2 mm in diameter and the energy density was 20 J/cm$^2$.

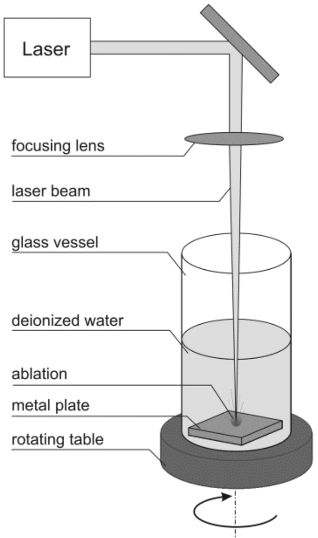

**Fig.1** Scheme of the experimental setup used for production of titania nanoparticles.

The route for synthesis was divided into two stages. At first, the titanium metal plate (99.99%) was placed in a glass container filled with deionized water (7 mL, 5 μS) and irradiated with laser beam for 60 min. During irradiation the glass vessel was rotating to avoid a crater formation in the metal plate, as a result of ablation. Finally, white colloid of titania nanoparticles was obtained. In the second stage, the titanium target was replaced with the platinum plate (99.99%), and the ablation process was continued for a defined time: 2, 5 and 10 min. As a result, we obtained stable colloids of titania nanoparticles modified with variable content of Pt, which depend on the duration of Pt ablation process. According to X-ray photoelectron spectroscopy (XPS) analysis, platinum content equals 0.1%, 0.35% and 0.57% when Pt target was irradiated for 2, 5 and 10 minutes respectively. The obtained colloid samples were described as: (0.1Pt)-$TiO_2$, (0.35Pt)-$TiO_2$, (0.57Pt)-$TiO_2$, depending on the platinum content.

Samples of pure and Pt modified titania in a form of powder, after centrifugation (14000 RPM, 10 min.) of colloid and precipitate drying at 60°C for 6 h were characterized with the use of UV-vis, Raman, and X-ray photoelectron spectroscopy. Within 60 min. there was obtained 3.1 mg of pure titania powder.

The UV-vis reflectance spectra of powders were measured with a dual beam UV-vis spectrophotometer (Lambda 35, Perkin-Elmer) equipped with diffuse reflectance accessory. The spectra were registered within the range of 200-700 nm, with the scanning speed of 120 nm/min. Bandgap values were calculated from the corresponding Kubelka-Munk function, $F(\mathrm{R})$, which is proportional to the absorption of radiation, by plotting $F(\mathrm{R})^{0.5}E_{\mathrm{ph}}^{0.5}$ against $E_{\mathrm{ph}}$, where $E_{\mathrm{ph}}$ is photon energy.[16]

The Raman spectra were recorded by a confocal micro-Raman spectrometer (InVia, Renishaw) with sample excitation, by means of an argon ion laser emitting at 514 nm.

XPS analyses of samples were carried out with the use of a multichamber ultra high vacuum (UHV) system, (Prevac). Before analysis the investigated samples did not undergo any preliminary chemical treatment. Powder samples, after their compression, were analyzed in the form of tablets. Then the samples were immobilized on a molibdene holder and degassed at a room temperature to constant pressure ~$5\cdot10^{-8}$ mbar in the leading lock of the UHV system. Afterwards, the samples were introduced into the analytic chamber of UHV system and specific XPS analysis took place. A monochromatic hemispheric analyser (R4000, VG Scienta) was used as an excitation source. X-ray radiation from Al anode (Kα = 1486.6 eV, U = 12 kV, I = 30 mA) was used. During spectra collection, the samples were irradiated by low-energetic electron source EFG (Electron Flood Gun, E = 2V, 1e = 200 μA) in order to eliminate electrostatic charging of specimens. In the analytic chamber, during spectra collection, the vacuum was at the level of $5\cdot10^{-9}$ mbar or better. The parameters of XPS spectra registration were as follows: a) for survey spectrum: Pass Energy 200, step: 300 meV b) for high resolution spectrum: Pass Energy 50, step: 100 meV.

The CasaXPS program was used for XPS spectra processing and quantitative analysis of the surface of the examined samples. In order to normalize spectroscopic measurements, X axis (binding energy, $E_{\mathrm{bin}}$) from XPS spectrum was calibrated for peak characteristics of neutral carbon 1s ($E_{\mathrm{bin}}$ = 284.7 eV).

Transmission electron microscopy (TEM) images were taken on a JEM-ARM200F (Jeol) Schottky field emission gun (FEG), and high resolution transmission electron microscope operated at an accelerating voltage of 200 kV. For transmission electron microscopic examination, the colloid was dropped onto a copper grid covered with a carbon-coated collodion film (Ted Pella, Inc.) and evaporated in the air at room temperature. Photocatalytic efficiency of pure titania and titania modified with platinum was determined by studying methylene blue (MB) decomposition in an aqueous solution under an ultraviolet (UVA) lamp (365 nm) radiation. The radiation intensity measured at the solution level was 5 mW/cm$^2$ (Ophir). The initial methylene blue (MB) concentration was $1 \cdot 10^{-5}$ mol/dm$^3$. The amount of powder sample was 9.3 mg (21 mL of produced colloid) in a 30 mL of MB solution that gives 0.31 mg/ml of photocatalyst concentration. Prior to UV irradiation, the MB solution with titanium dioxide was kept in darkness for 30 min., allowing for adsorption-desorption equilibrium to be reached. Under UV irradiation and vigorous stirring, photodegradation of MB was continued for 300 min. Every 30 min. the concentration of MB after illumination was determined by a UV-vis spectrophotometer, using its characteristics absorption band at 665 nm. In order to compare photocatalytic activity of laser and chemically produced Pt-$TiO_2$, samples of titanium dioxide modified with different content of platinum were prepared also by chemical reaction according to Kim et al.[17] In general, the pure titania colloid obtained using LAL method was mixed with methanol (1M) and an appropriate volume of 5 mM chloroplatinic acid ($H_2PtCl_6$) to reach final concentration of Pt consistent with the amount of platinum present in the laser produced Pt-$TiO_2$ samples. Then, the solutions were irradiated with a 300 W UV lamp for 45 min. After irradiation, Pt-$TiO_2$ suspensions with different Pt content were centrifuged, washed and dried. Photodegradation of MB was investigated for chemically sensitized Pt-$TiO_2$ in the same conditions as for LAL produced modified titania.

## C Results and Discussion

### Raman

Figure 2 shows Raman spectra of pure $TiO_2$ and titania modified with Pt. We can observe bands typical for anatase crystalline phase: $E_{g(1)}$, $E_{g(2)}$, $B_{1g}$, $A_{1g}$ and $E_{g(3)}$.[1] The band corresponding to $B_{1g}$ mode, typically located at 519 cm$^{-1}$ is hardly visible, due to overlapping of $A_{1g}$ and $B_{1g}$ signals.[18] The position of $E_{g(1)}$ typically observed around 144 cm$^{-1}$ [19-21] is here registered in the range 150 - 160 cm$^{-1}$. Therefore, all of produced particles are characterized by the smaller size than materials obtained via chemical synthesis. Additionally, it can be seen that positions of the $E_{g(1)}$ active mode are different for each sample - for $TiO_2$ is 162.75 cm$^{-1}$, (0.1Pt)-$TiO_2$ is 153.61 cm$^{-1}$, (0.35Pt)-$TiO_2$ is 151.31 cm$^{-1}$, (0.57Pt)-$TiO_2$ is 150.94 cm$^{-1}$. This displacement in $E_{g(1)}$ signal to lower values of Raman shift is with accordance with increased duration of the second stage of ablation process when Pt loading. The red shift could be explained in terms of increase in size of the Pt-decorated titania particles in comparison to pure titania particles.[19,22] Increase in particle size may result from: a) deposition of Pt nanoparticles onto the titania surface or b) longer laser irradiation (i.e. sample (0.57Pt)-$TiO_2$ underwent 10 minutes longer irradiation than $TiO_2$ colloid) that could lead to particle conglomeration. However, irrespectively on platinum loading the colloids remains stable for a long time.

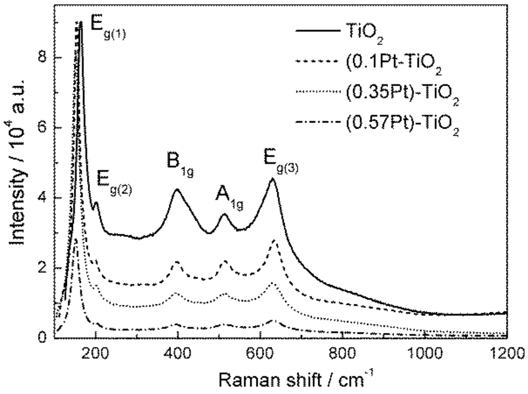

**Fig.2** Raman spectra registered for pure and platinum modified titania.

### UV-vis spectroscopy

The absorbance curves and the Tauc plot are presented in the Fig. 3. By drawing the tangent to the slope, the intrinsic bandgap of pure and modified $TiO_2$ could be determined. The band gap energy for pure titania equals 3.16 eV, whereas for platinum modified $TiO_2$ we can observe a slight decrease in the value of the bandgap energy. For (0.1Pt)-$TiO_2$, (0.35Pt)-$TiO_2$, (0.57Pt)-$TiO_2$ bandgap energies equal 3.11, 3.07 and 3.02 eV respectively. Therefore, Pt deposition could significantly shift the activity towards a visible light region. Li *et al.*[23], Kim *et al.*[24] and Beck *et al.*[25] also confirmed the enhancement of visible optical absorption due to the presence of Pt, $Pt(OH)_2$ and $PtO_2$, which has been proven by UV-vis reflectance spectra. This phenomenon is attributed also to overlapping of the origin of the band gap excitation of a $TiO_2$ particle with the plasmon band of Pt.[26]

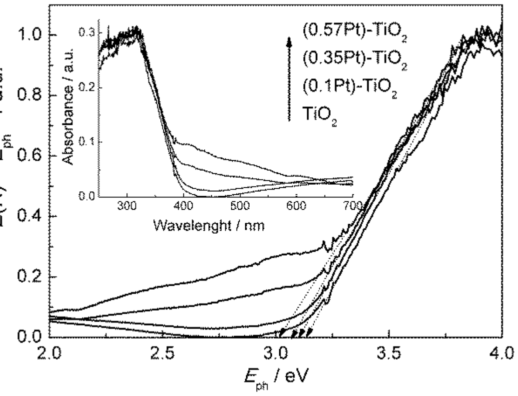

**Fig.3** The Tauc plot for pure and platinum modified titania, inset: absorbance spectra.

Another explanation of visible light absorption is that some energy levels could be generated within the band gap of titania by the dispersion of Pt nanoparticles and the $TiO_2$ matrix. The surface state between Pt and titania nanoparticles (see TEM section) could play an important role in producing lower energy levels localized between $TiO_2$ valence and conductance bands. Some reports have confirmed the presence of defect energy levels attributed to Ti (III), that act as color centres that provide channel within the bandgap allowing visible light absorption.[27] According to Zhu et al.,[28] apart from Ti (III), between conduction and valence band there could be located many energy levels: below Fermi level - for trapped electrons and under the conduction band - for localized states (shallow traps). The identification of such energy levels could be determined using time-resolved transient mid-IR absorption spectra with midgap excitation energy scanning. On the other hand, according to Ravichandran et al.[29] the addition of platinum and following UV irradiation causes significant changes to the absorption spectrum of $TiO_2$ resulting in high absorbance above 400 nm. Since this band does not appear in Pt-$TiO_2$ spectra, the red shift may not be due the surface plasmon absorption. Hence, the extended absorption resulted from band gap absorption. The absorbance in the visible region for the metalized system shows that lower energy transitions are possible. This is because the metal clusters give rise to localized energy levels in the band gap of $TiO_2$ into which valence band electrons of $TiO_2$ are excited at wavelength longer than 370 nm. According to Ravichandran et al.[29] if equal sized metal clusters are formed, it will lead to constant absorption in the visible region corresponding to the excitation from the valence band of $TiO_2$ to the occupied level of metal cluster. Since we observe gradual decrease in absorption from 340 to 650 nm in the absorption spectrum of Pt-$TiO_2$ materials, the metal clusters in the catalyst are not of equal size.

## TEM

The particle morphology and structure of pure titania and titania modified with different amount of platinum were further investigated by TEM (Fig. 4). The particles in two TEM images: 4 a) and 4 c) can be recognized as perfect rounded particles in projection, due to the fact that particles have a spherical shape. This almost perfect spherical shape seems to be common to all particles regardless of duration of the second stage of the preparation process. Small platinum nanoparticles (some of these particles are indicated by the arrows in the Fig. 4c) were observed on the $TiO_2$ surface. According to Qamar *et al.*[30] in the case of Pt modified titania there is no chemical bonding between Pt and titania surface but platinum remains adhered onto the oxide surface by a interaction called strong metal support interaction (SMSI). SMSI is attributed to overlapping of the orbitals (occupied) from deposited Pt and unoccupied d orbitals of the $TiO_2$ support.[31,32] The mechanism of interaction (junction) between noble metal nanoparticles and metal oxide was also discussed by Zhang *et al.*[9] and Sylvestre *et al.*[33] According to Zhang *et al.,*[9] noble metal nanoparticles produced in the process of laser ablation in liquid are partially oxidized. Hydroxyl groups from aqueous solution absorb on freshly produced metal nanoparticles and form negatively charged surface what stabilize the colloid.[34] That surface capped with -OH groups is supposed to easily interact with other materials, *i.e.* metal oxide to form NP-metal oxide hybrid structures.

The diameter of titania particles was found to be within the range of 5 - 30 nm; for Pt particles, the diameter ranges from 3 to 20 nm. Figures 4 b) and 4 d) present HRTEM images of an individual titania and platinum particle respectively. Lattice fringes are clearly visible, which proves crystallinity of particles obtained. From the local magnified image, we can thus determine the fringe separation of 0.17 nm and 0.23 nm for titania nanoparticles. They correspond to the lattice distance of (105) and (004) planes of the anatase structure respectively.[35] The interplanar angle between (105) and (004) is equal to 30° that is similar to HRTEM analysis of anatase phase given by Barreca *et al.*[35] Zone axis in the direction lying of these two planes: (105) and (004) is given by [0,-4,0]. The fringe spacing observed for Pt nanoparticle equals 0.22 nm and 0.196 nm that is characteristic for (111) and (200) Pt lattice spacing.[36,37] Because adjacent lattice fringes of 0.196 is attributed to (200), Pt nanoparticles are bounded by (100) facets .[37] The appearance of (100) and (111) is regarded as fcc cubo-octahedral shape.[38]

As it was mentioned in UV-vis spectroscopy analysis that interfacial interaction between Pt and $TiO_2$ nanoparticles could could be responsible for generation of the lower energy levels within titania bandgap, therefore epitaxial relationship between Pt and $TiO_2$ nanoparticles was determined: (111) Pt || (105) $TiO_2$ and (111) Pt || (004) $TiO_2$ (see Fig. 4d).

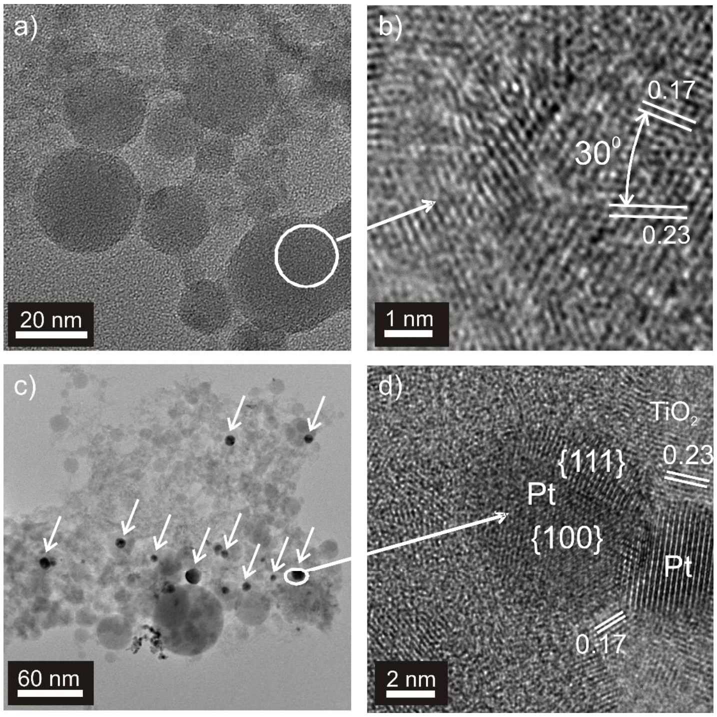

**Fig.4** TEM images of: a) pure titania, c) titania modified with platinum (0.35Pt)-$TiO_2$ and HRTEM images of b) $TiO_2$ and d) platinum nanoparticles deposited onto the titania surface.

## XPS

Figure 5 shows XPS spectra of Ti2*p*, O1*s*, C1*s* and Pt4*f* core levels registered for (0.57)-$TiO_2$. Inside the three of them, there are spectra for the corresponding orbitals obtained for pure titania. The high-resolution XPS spectrum of Ti2*p* was deconvoluted into two dublets described as A and B. For Pt modified titania, the first dublet: $Ti2p_{3/2}A$ (459.0 eV) and $Ti2p_{1/2}A$ (464.8 eV) corresponds to Ti(IV) and the second one: $Ti2p_{3/2}B$ (457.6 eV) and $Ti2p_{1/2}B$ (463.4 eV) is assigned to Ti(III).[39] Almost the same positions of deconvoluted peaks were obtained for the spectra registered for other modified titania samples and pure titania as well. For all the examined samples: pure and Pt-modified, the atomic concentration of Ti(IV) is over 95%. The presence of a small amount of Ti(III) sites was reported and is equal to 1.93% ($TiO_2$), 2.52% (0.1Pt-$TiO_2$), 3.17% (0.35Pt-$TiO_2$), 3.88% (0.57Pt-$TiO_2$) of total titanium quantity. As it could be seen, the amount of the Ti(III) slightly increase with the amount of deposited platinum. According to Li *et al.*[23] the trivalent titanium arise from the deposition of Pt onto the surface of $TiO_2$ and the formation of Ti(III) implies that the integration between Pt and the $TiO_2$ matrix occurred during photoreduction. Thus, it shows that there is a deficiency of oxygen and an increase of $O_2^-$ anions that prevents recombination of electron-hole pair on the surface. The presence of a small amount of Ti(III) sites plays an important function in the photocatalysis with $TiO_2$.[40,41] Sakthivel *et al.*[42] concluded that defect sites of the $TiO_2$ surface are necessary for the photooxidation of pollutants. These defect sites are identified as Ti(III), and are essential for adsorption and photoactivation of oxygen.

The carbon C1*s* peak was deconvoluted into four separated Gaussian distributions. In the spectrum of (0.57Pt)-$TiO_2$ the highest peak at 284.7 eV was originated from C-C or C-H bonds.[43,44] This peak, typical for graphitic carbon,[45] as it was mentioned in experimental part, was used for calibration of the XPS spectra. The peak observed at 286.0 eV corresponds to C-O bonds.[46] The last two bands located at 287.6 eV and 289.4 eV are attributed to C=O[47] and $-CO_3$ arrangement respectively.[48] They are typical for adsorbed carbon on the sample.

It should be noted that the intensity of registered spectrum for carbon is much smaller in comparison to the spectrum of C1*s* core level obtained for the titania prepared by laser ablation in liquid, with poly-(vinylpyrrolidone) as the organic surfactant-assistance.[49]

The O1s spectra within pure and modified titania can be principally assigned to the bulk oxygen (Ti-O-Ti linkages)[50] and surface adsorbed hydroxyl group (Ti-OH),[51] with the respective binding energy of 530.6 eV and 532.0 eV observed for (0.57Pt)-$TiO_2$ sample. The atomic concentration of oxygen related to the titania lattice is about 85%, whereas the oxygen present in -OH groups state for 10%. The rest of oxygen is represented by the peak located at 532.9 eV that could be assigned to oxygen in molecular water[52] or C-O- bond.[53] Similar position of these three singlet peaks and oxygen distribution between bulk and surface species are observed for all the examined samples. Fig. 5 also presents the spectrum registered for platinum 4*f* orbital of (0.57)-$TiO_2$, with deconvoluted peaks. Similar spectra were observed for other platinum modified samples. On the basis of fitting procedure there were distinguished three dublets of Pt4$f_{5/2}$ and Pt4$f_{7/2}$.

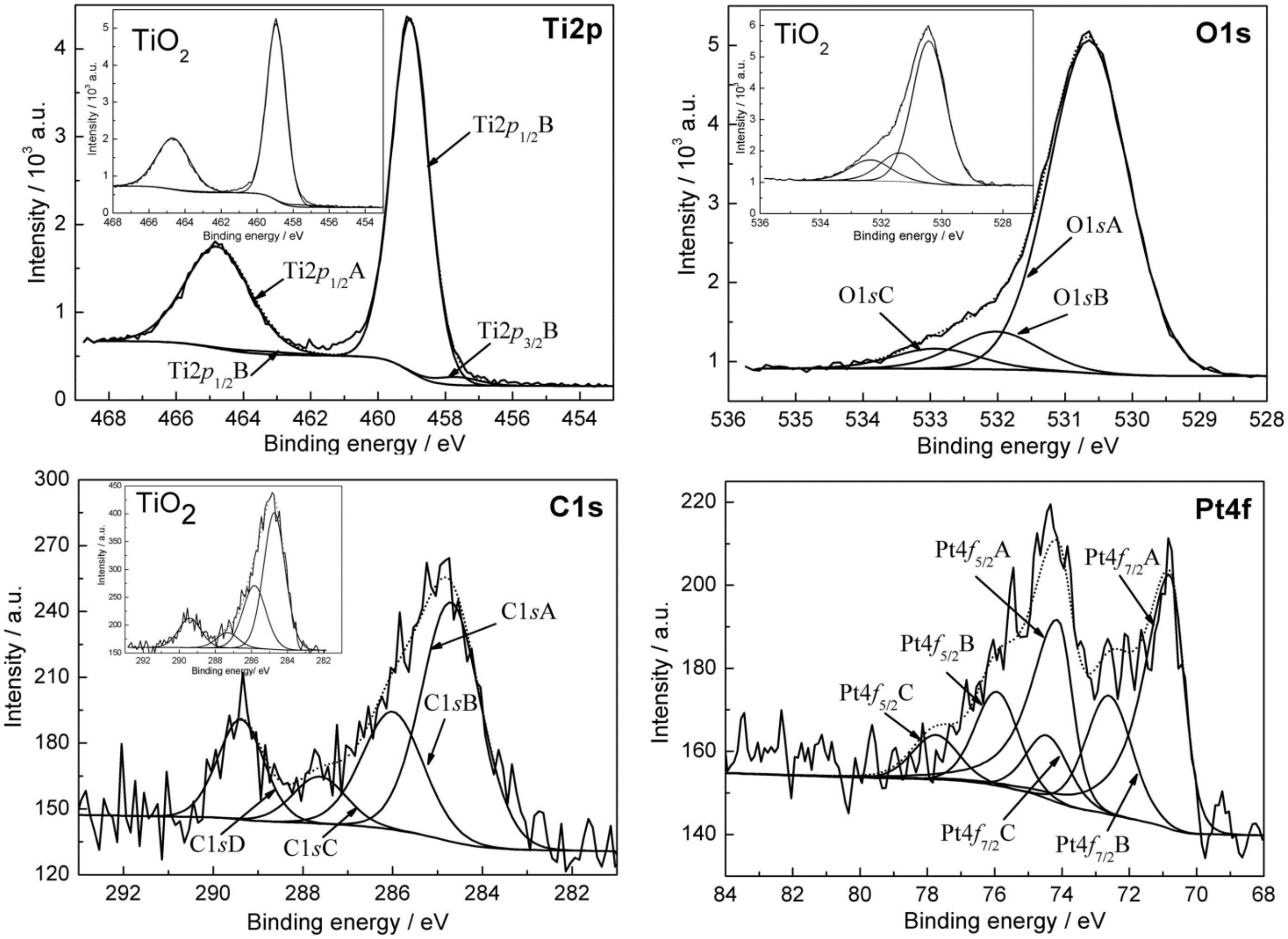

**Fig. 5** XPS spectra for Ti2*p*, O1*s*, C1*s*, Pt4*f* core levels registered for (0.57)-$TiO_2$ powder sample, inset: spectra for pure $TiO_2$ (dotted line – fitting spectrum).

Dublet A is assigned to Pt(0), B to Pt(II) and dublet C corresponds to Pt(IV).[54] The atomic concentration of Pt oxidation states is different with regard to all the examined samples, and is presented in Table 1. It should be noted that the presence of metallic Pt is regarded as oxidation state with higher activity than Pt(II) and Pt(IV).[55]

On the basis of X-ray photoelectron spectroscopy surface composition listed in Table 1 was calculated. Taking into account that approximately 85% of oxygen is built in the lattice, the O/Ti ratio roughly equals 2 for all the prepared samples. As for the Pt modified titania powders, platinum content equals 0.1, 0.35 and 0.57 when Pt target is irradiated for 2, 5 and 10 min. respectively. Summarizing, with the increased irradiation time of Pt plate during the second stage of ablation process, the atomic concentration of platinum grows.

**Table 1** Atomic concentration of each element and Platinum phase for modified titania.

| | **Atomic content / %** | | | | **Atomic content of Pt phase / %** | | |
|---|---|---|---|---|---|---|---|
| **sample** | **O1s** | **Ti2p** | **C1s** | **Pt4f** | **Pt(0)** | **Pt(II)** | **Pt(IV)** |
| $TiO_2$ | 61.61 | 24.55 | 13.84 | **0** | 0 | 0 | 0 |
| (0.1Pt)-$TiO_2$ | 59.72 | 25.47 | 14.71 | **0.10** | 0 | 53.89 | 46.11 |
| (0.35Pt)-$TiO_2$ | 62.00 | 25.91 | 11.74 | **0.35** | 72.48 | 12.06 | 15.46 |
| (0.57Pt)-$TiO_2$ | 63.12 | 26.08 | 10.23 | **0.57** | 58.39 | 27.78 | 13.83 |

### Mechanism description

The mechanism of metal-oxide formation by laser ablation at liquid-solid interface is a complex process.[56] According to previous works on laser ablation in a liquid medium, during the first stage of interaction between the laser beam and the metal surface a hot plasma plume over the target surface is generated.[57,58] This phenomenon results from intensive evaporation of metal, as it is observed in the case of pulsed laser ablation in gas phase or vacuum. Since the expanding plasma is limited by a liquid medium, the shock wave created in front induces elevated pressure and a further increase of plasma temperature. The surrounding water molecules reach the temperature higher than the boiling point.[59] The vapour pressure in the vicinity of a metallic target is generally assumed to be the liquid vapor pressure at the target temperature.[60] This effect causes formation of bubbles, which can be observed during the ablation process. The active species: titanium ions, atoms and clusters produced during the ablation process interact with the water molecules at the plasma/liquid interface and form nuclei of oxide/hydroxide via rapid quenching.[4] Chemical reaction products such as titanium dioxide or hydroxide molecules could aggregate as fast as the molecules are supplied. The initially aggregated clusters thus serve as a nuclei; they rapidly quench into the liquid solution together with other radicals or ions such as •OH or $H^+$.[56]

In the next step, after titania colloid production, Ti plate was replaced by platinum target and the ablation process was continued. As it was reported by other authors in case of gold nanoparticles production during laser ablation in water[9] the Au atoms on the surface of freshly prepared nanoparticles are partially oxidized and interact with OH- groups from aqueous solution. The -OH capped nanoparticles surface is supposed to easily interact with other materials. It can be expected, that similar phenomena occurs in case of platinum nanoparticles and the Pt-nanoparticles produced in the titania colloid can be easily connected by chemical interaction to the titania nanoparticle utilizing hydroxide surface groups present on titania surface. Additionally during the second stage of ablation process the part of laser energy is absorbed by titania colloidal solution. Similarly, the two-stage ablation process was used for formation of bimetallic Al-Au particles, where Au plate was ablated in a freshly prepared Al colloid. That procedure resulted in connection of gold to already formed aluminum clusters.[61] It is also known, that irradiation of the mixture of colloidal solution of individual metals allows for obtaining Au-Ag alloy.[61] Thus it is assumed that Pt atoms and clusters appearing in our experiment are active enough to bind themselves to the surfaces of previously prepared $TiO_2$ nanoparticles; partial absorption of laser energy by colloid solution can influence this process.

The obtained colloids of titania nanoparticles are stable for a few weeks and no precipitation process has been observed. Such stability in water is achieved because laser generated particles are charged and repel each other.[61]

### Photocatalytic properties

Photocatalytic degradation of methylene blue in aqueous solution conducted with using different samples was carried out as shown in Figure 6. Obviously, efficiency of the titania catalyst could be improved by the presence of Pt nanoparticles in the case of laser produced and chemically sensitized Pt-$TiO_2$ as well. The catalytic efficiency for MB degradation was improved by 30% with (0.57Pt)-$TiO_2$ in relation to pure titania, after 300 min. A still more pronounced effect is observed for shorter times, e.g. after 150 min. of photocatalysis experiment we observed the degradation of methylene blue at the level of only 35% for pure titania but 57%, 69% and 82% for (0.1Pt)-$TiO_2$, (0.35Pt)-$TiO_2$ and (0.57Pt)-$TiO_2$, respectively. The observed kinetic constant (pseudo-first-order kinetics) of pure $TiO_2$ was 3.3 ($10^{-3}$ $min^{-1}$) and for $TiO_2$ modified with 0.1, 0.35 and 0.57 at. % of Pt was 6.4, 8.1 and 11.1 ($10^{-3}$ $min^{-1}$) respectively. The influence of platinum presence onto the titania photocatalytic properties are in correspondence with other studies, where Pt-$TiO_2$ was verified as a photocatalytic material in contact with 4-chlorophenole,[26] methylene blue[14]**Error! Bookmark not defined.** or o-cresol[39] and degradation efficiency was higher than that observed for unmodified titanium dioxide. However, there is observed big difference in degradation efficiency and following kinetic constant between $TiO_2$ and Pt-$TiO_2$ materials unlike to chemically obtained platinum modified titania.[14,23] Furthermore, particles produced by laser ablation exhibit higher photocatalytic activity that chemically sensitized Pt-$TiO_2$. According to Zhang et al.[9], that phenomenon could be attributed to presence of strong interaction between laser loaded Pt nanoparticles on the titania surface.

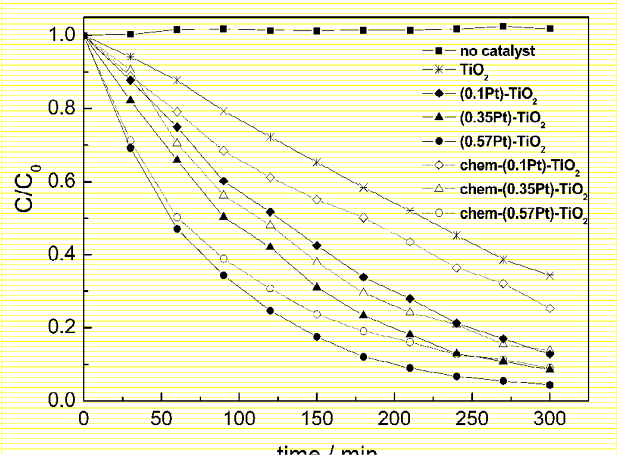

**Fig. 6** Degradation curves of MB over pure, laser and chemically sensitized Pt-modified titania.

Such increase in kinetic constant registered for Pt-$TiO_2$ allow to conclude that proposed method, based on laser ablation in liquid leads to more active Pt modified titania towards degradation of organic contamination under UV illumination than chemical synthesis. It should be emphasized that because laser generated material is free of toxic surfactants which impure the nanoparticle surface we could synthesize one of the purest nanoparticles which can be used for bioconjugation, surface enhanced Raman spectroscopy (SERS) or catalysis. Additionally, proposed method does not require any thermal treatment at high temperature that is usually last stage of chemical synthesis of $TiO_2$ in order to eliminate organic residues from titania precursors and change the crystalline phase from amorphous to crystalline one. The particles generated using LAL are stable in water because laser generated particles are charged and thus obtained colloids are not inhalable. That leads to an improved occupational safety for product handling. From the practical point of view, the absence of additional thermal annealing/purification stages enables integration of LAL with other laser assisted processes (*i.e.* surface modification, substrate processing that will serve as surface for nanoparticles immobilization).

It is commonly known that under UV-light excitation, the electrons of the $TiO_2$ valence band are excited to the conduction band. When Pt nanoparticles are loaded onto the titania surface, the heterojunction (Schottky junction) is formed, where conduction band electrons are transferred to the Pt particle.[62] This occurred because Pt has higher work function and thus platinum particles acts as a charge scavenger, effectively blocking recombination of electron-hole pairs.[1,63] Therefore, as the given results suggested, the photocatalytic activity of $TiO_2$ could be remarkably enhanced by modification with the use of platinum nanoparticles.

## Conclusions

To summarize, we have obtained colloidal Pt modified titania in deionized water using laser ablation in a two-step process. $TiO_2$ particles modified with platinum were produced by laser ablation from a platinum plate immersed in a freshly prepared pure titania colloid. That $TiO_2$ colloid was also obtained with the use of laser ablation process, where Ti metal plate was placed in deionized water. The proposed preparation method is quick, simple and does not require any additional surfactants/polymers or purification steps, which makes this synthesis much simpler in comparison to a conventional chemical synthesis. Furthermore, proposed method does not require any thermal treatment at high temperature in order to eliminate organic residues from titania precursors and change of the phase from amorphous to crystalline one. The obtained particles are almost perfect spheres in shape with the nano-size diameter. High resolution TEM images analysis identified Pt-modified titania material as polycrystalline anatase structure with fcc cubo-octahedral Pt. Furthermore, Raman spectroscopy measurements identified crystalline phase of titania powders as anatase. The titania modified with Pt has a narrower bandgap than pure $TiO_2$. X-ray photoelectron spectroscopy allowed for characterization of oxidation states of atoms, i.e. titanium compounds of oxidation states +III and +IV were found. Furthermore, the registered XPS spectra confirmed the presence of platinum at titania nanoparticles.

New materials were shown to be efficient photocatalysts for the degradation of the methylene blue dye. The Pt modified titania nanopowder showed a higher photocatalytic activity in comparison to pure $TiO_2$, *i.e.* in the presence of (0.57Pt)-$TiO_2$ after 5 h 95% decomposition of MB was observed, while for pure $TiO_2$ the degradation of MB did not exceed 65%. Moreover high difference in kinetic constant value between Pt-$TiO_2$ and $TiO_2$ produced by LAL unlike to chemically synthesized materials shows that laser assisted modification by platinum leads to more UV-active Pt-$TiO_2$ than traditional synthesis.

Further research concerning the influence of laser parameters and additional stage of post-ablation irradiation on the final colloid will be conducted.

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