



Modification of TiO₂ nanoparticles through lanthanum doping and PEG templating

Marija Milanović*, Ljubica M. Nikolić

Department of Materials Engineering, Faculty of Technology, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

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Abstract

Pure and lanthanum doped titania nanopowders were synthesized through a room temperature sol-gel method using a template of polyethylene glycol (PEG). The progress of the synthesis in terms of phase formation and size of nanoparticles was monitored by X-ray diffraction, FTIR spectroscopy and SEM analysis. After calcination at 450 °C in air, the results have shown the presence of small particles crystallized predominantly in the form of anatase phase, with significant agglomeration. Nitrogen adsorption-desorption measurements confirmed that all prepared powders are mesoporous with an average pore diameter in range 3.1–3.8 nm. The addition of lanthanum ions leads to the nanopowders with the highest specific surface (BET) area (203 m²/g). The obtained powders were compared to TiO₂ prepared without a template.

Keywords: titania nanopowder, anatase, lanthanum, PEG, mesoporous

I. Introduction

Nanostructured titania is one of the most studied semiconducting materials from fundamental and practical point of view, due to their excellent properties useful in many applications such as: optical, sensors and solar devices, photocatalysts, photoconductors, biomaterials etc. These applications rely upon the intrinsic properties of titania, which are governed by the extent and nature of its crystalline phase (anatase, rutile, brookite). Since anatase is more suitable than rutile in many fields of applications (monitoring some gases, pollutant photodegradation, etc.) it is necessary to stabilize anatase phase at higher temperatures and hinder anatase to rutile transformation [1,2]. The addition of different concentrations and type of dopants can be a useful way to prevent anatase to rutile transition and to inhibit its particle growth [3,4]. Lanthanum is one of the rare-earth metal elements investigated widely for this purposes. Lanthanum ion with its 4f electron configuration can interact with the functional groups with its f-orbital. This can increase the adsorption of organic pollutants on the surface of photocatalyst and it is beneficial for the improvement of the photocatalytic activity [5]. In this pa-

per, we attempted to dope lanthanum into TiO₂ by sol-gel method.

In addition to the polymorph of titania, the crystallite size, the specific surface area and porous structure are crucial parameters for high performance applications [6]. If modification of chemical and physical properties of a material is possible, a better control of chemical reactivity and/or stability for a given application can be achieved. In recent years, various modifications have been developed to improve the morphology, surface area and porosity of titania nanomaterials. Amorphous mesoporous titania with a periodic ordering of the pores was first reported in 1995 via a modified sol-gel process applying an alkyl phosphate surfactant [7]. Since then, there have been many reports on the synthesis of mesoporous titania by addition of stabilizing and/or structure directing agents, such as phosphates, amines, ionic and non-ionic surfactants and block copolymers [8–10]. In this paper, the preparation of such modified nano titania was achieved through a room temperature sol-gel method, employing a polyethylene glycol, PEG as a structure directing agent. Zhang *et al.* [11] reported that PEG template acted as a pore forming reagent in the sol-gel preparation of TiO₂-Al₂O₃ binary oxides. Jianguo *et al.* [12] reported that transparent TiO₂ thin films with different surface structures have been prepared from

*Corresponding author: tel: +381 21 485 3758
fax: +381 21 450 413, e-mail: majam@uns.ac.rs

solutions containing polyethylene glycol (PEG) via the sol-gel method. Preethi *et al.* [13] combined the conventional PEG with a bio-template (chitosan) in preparation of mesoporous nano titania.

In the presented paper, pure and La-doped titania nanopowders were synthesized through a room temperature sol-gel method. The influence of lanthanum doping on the phase transformation and stability of the anatase phase was investigated. To obtain the mesoporous structure, the polyethylene glycol, PEG was envisaged as a templating agent in both pure and lanthanum doped titania particles. The effect of PEG template on the size, porosity and surface area of the resulting titania was studied against the characteristics of titania prepared without template.

II. Experimental

2.1. Materials

Tetrabutyl-orthotitanate (TBOT), polyethylene glycol with the molecular weight of 600 (PEG), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and isobutanol were purchased from Fluka Chemicals. All the chemicals are of analytical grade and were used without further purification. Distilled water was used throughout the experiments.

2.2. Sample preparation

The preparation scheme of TiO_2 nanopowders is shown in Fig. 1. Titania nanopowders were synthesized by a sol-gel method at the room temperature. The precursor solution A was prepared by mixing the tetrabutyl orthotitanate with isobutanol. The hydrolysis solution B was prepared by mixing distilled water with isobutanol and nitric acid. Then solution B was added drop by drop into solution A under vigorous stirring and additionally stirred for half an hour to obtain solution C. In a typical procedure, the reaction was carried out using TBOT : $i\text{-C}_4\text{H}_9\text{OH}$: HNO_3 : H_2O molar ratio of 1 : 5 : 0.5 : 2, and pH around 3. In that way, the pure TiO_2 sol was obtained.

In order to investigate the effect of La^{3+} and PEG in the preparation of TiO_2 nanopowders, we have prepared two additional solutions: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as a source of La^{3+} was dissolved in isobutanol forming the solution D and PEG was dissolved in isobutanol forming the solution E. These solutions were added first separately to the above mixture during the sol-gel reaction, as presented in the Fig. 1, and then simultaneously. In that way three following sols were obtained: TiO_2 sol doped

with La^{3+} , TiO_2 sol with PEG and TiO_2 sol doped with La^{3+} with addition of PEG (Table 1). The molar ratio of PEG/TBOT was 0.04 and the ratio of La/Ti was set to 6 at. %.

All the obtained sols were translucent, homogeneous and bright yellow. It should be emphasized that prepared under these conditions, sols have shown very good stability (stable for 15 days), which could be very useful for production of titania coatings where a long term stability of the titania sol is needed in order to achieve an acceptable repeatability.

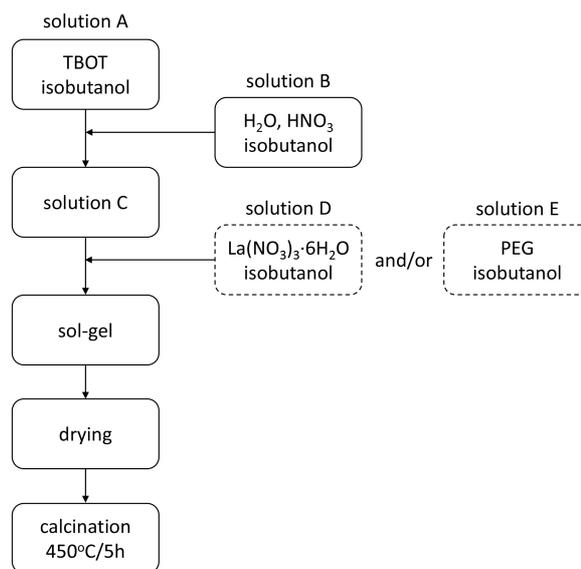


Figure 1. Flowchart representing the preparation of TiO_2 nanopowders using sol-gel method

After aging for 5 days, the sols were dried slowly at 40°C for 3 days, then at 60°C for 2 days and finally at 120°C during 1 day. After being dried, the as-synthesized powders were subjected to the thermal treatment at 450°C for 5 h. The sample notations are shown in Table 1.

2.3. Characterization

The crystallinity and the phase composition of the obtained titania nanopowders were determined by X-ray diffraction (XRD) using Rigaku MiniFlex 600 diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). X-ray diffraction patterns were recorded in the range $10\text{--}60^\circ$ at a scan rate of $0.03^\circ/\text{s}$. The average crystallite size of anatase was determined according to the Scherrer's equation

Table 1. Synthesis conditions and sample notations of the obtained nanopowders

Sol composition	As-synthesised powders	Calcined powders	PEG/TBOT [mol]	La/Ti [at.%]
TiO_2	T	T-450	0	0
TiO_2 + PEG	TP	TP-450	0.04	0
TiO_2/La	TL	TL-450	0	6
TiO_2/La + PEG	TLP	TLP-450	0.04	6

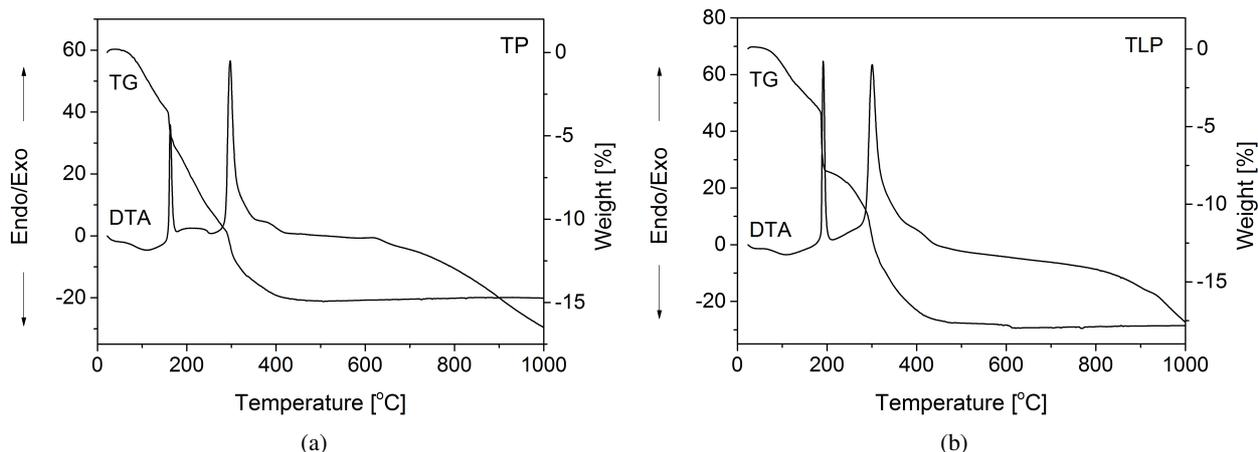


Figure 2. DTA/TG of as-synthesized titania nanopowders: a) TP and b) TLP

using a FWHM of the 101 reflection. The anatase content of samples was calculated from equation [14]:

$$W_A = \frac{K_A \cdot I_A}{K_A \cdot I_A + I_R + K_B \cdot I_B} \quad (1)$$

where W_A represents the mass fraction of anatase and I_A , I_B and I_R are the integrated intensities of the anatase 101, brookite 121 and rutile 110 peaks and K_A and K_B are two coefficients and their values are 0.886 and 2.721, respectively. The size and morphology of particles in the samples were observed by a scanning electron microscope (SEM JEOL 6460LV). FTIR measurements of the samples were carried out on Nicolet-Nexus 670 spectrophotometer. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA, Bähr, STA 503) with a heating rate of 10 °C/min from 20 to 900 °C in air atmosphere was used to study the thermal behaviour of the as-synthesized (dried) powders. Specific surface areas of TiO₂ powders were measured by nitrogen adsorption at 77 K (Quantachrom Autosorb-3B) using Brunauer-Emmett-Teller (BET) method. The pore size distribution was derived from the N₂ desorption isotherm using the BJH method.

III. Results and discussion

The TG-DTA curves of the as-synthesized (dried) titania nanopowders treated with PEG, TP and TLP are shown in Fig. 2. Thermogravimetric analysis was performed in order to replicate the calcination conditions for the as-synthesized samples. The characteristics of thermal behaviour for the investigated samples are very similar, as shown in Fig. 2. For both samples, there is a small endothermic peak around 100 °C, attributed to the evaporation of adsorbed water and isobutanol. This peak is accompanied with the mass loss of about 4 wt.% in both samples. In the temperature range from 150 °C to 450 °C, the samples show obvious weight loss of about 11 wt.% (TP) and 14 wt.% (TLP). The DTA curve shows two main exothermic peaks in this region. The first exothermic peak, with its maximum

at 162 °C (TP) and 191 °C (TLP), is very sharp and narrow, and is attributed to the combustion and the release of organic residues. The second sharp and narrow exothermic peak, at around 300 °C in both samples, could be attributed to the crystallization process of titania nanopowders simultaneously with further removal of organic compounds that would explain the weight loss. The total weight loss measured from the TG curve was 14.8 wt.% for TP and 17.8 wt.% for TLP sample. TG curves show that weight loss above 450 °C is negligible. Therefore, this temperature was chosen as the calcination temperature for titania nanopowders. During this process the colour of TiO₂ powders turned from yellow (as-synthesized) to white.

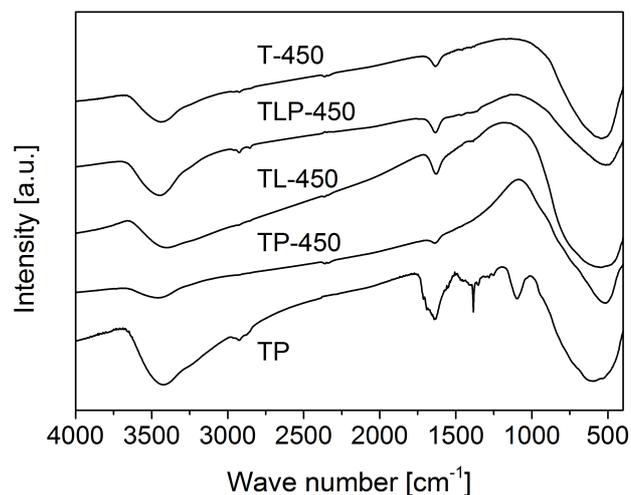


Figure 3. FTIR spectra of the as-synthesized titania nanopowder treated with PEG, TP and all titania nanopowders calcined at 450 °C

The FTIR spectra of the as-synthesized titania nanopowder treated with PEG, TP and all titania nanopowders calcined at 450 °C for 5 h are shown in Fig. 3. The spectra indicate that after heat treatment, PEG is completely removed from the powders since the characteristic bands at around 1100 cm⁻¹ and 1300 cm⁻¹

that originate from C–O–C bonds in PEG [15,16], are not present in the calcined titania nanopowders. The peak at 1107 cm^{-1} is characteristic for stretching vibration of ether oxygen group [17]. The peaks located at around 3400 cm^{-1} and 1650 cm^{-1} in all samples are assigned to the stretching and bending vibrations of OH groups. The difference in the position and shape of the band characteristic for Ti–O vibrations ($450\text{--}800\text{ cm}^{-1}$), indicates the different degree of crystallinity as well as the phase composition of the investigated samples [18].

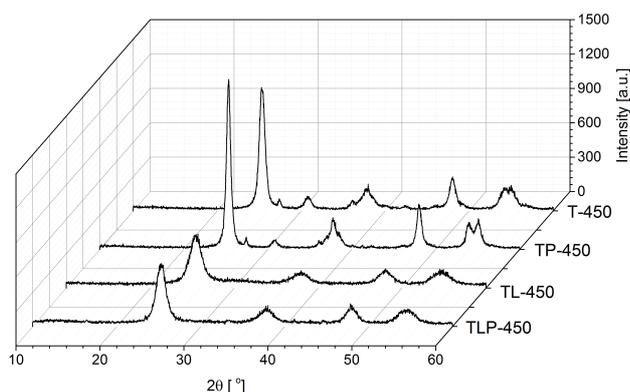


Figure 4. XRD diffractograms of titania nanopowders calcined at 450 °C

Table 2. Phase composition (from XRD) and crystallite size (anatase) of titania nanopowders calcined at 450 °C

Sample	Phase composition ^a	Anatase phase content [%]	d_{anatase} [nm]
T-450	A + R + B	68	10.6
TP-450	A + R + B	80	16.3
TL-450	A	~100	4.1
TLP-450	A	~100	6.1

^aA-anatase, R-rutile, B-brookite

Figure 4 shows the XRD patterns of titania nanopowders after heat treatment at 450 °C for 5 h. Anatase phase with the characteristic peak at $2\theta \sim 25.3^\circ$ is dominant

in all the samples. The pure titania nanopowder, T-450, besides the anatase phase consists of rutile and brookite phases, which characteristic peaks appear at 27.4° and 31° , respectively. These phases are also present in the titania powder treated with PEG, TP-450, but according to the peak widths, it could be noticed the increase of the particle size in this sample. The average particle sizes of the investigated powders estimated by Scherrer's equation are presented in Table 2, together with the phase composition and anatase phase content. From the presented results, two distinguished phenomena could be highlighted. The first, addition of PEG does not affect the phase composition, but the phase content and the particle sizes are rather changed. The anatase mass fraction of TiO_2 particles increased noticeably in PEG treated particles. With the addition of PEG, the peak intensity of anatase increases gradually, indicating that PEG significantly promotes the crystallization of this TiO_2 phase. Since, there is an ether oxygen in PEG chain, that can interact with the metal ions at the molecular level, PEG could display the effect on hydrolysis and polycondensation reactions of sol-gel process and therefore on the crystallization of TiO_2 [19]. Priya *et al.* [16] investigated the structural role of PEG in the formation of nanocrystalline anatase at low temperature and showed that PEG undergoes a nucleophilic substitution reaction replacing butoxy groups in tetrabutyl-orthotitanate. The binding of PEG with titanium and the orientation of the Ti–O bond in the polymers are in such a way that they favour the formation of anatase nanocrystals when PEG is removed. Also, the concentration of PEG and PEG/(water+alcohol) ratio are very important for controlling the particle size and shape of the obtained material [15,17]. Under the conditions set in this work, particles treated with PEG, the sample TP-450, are larger than the non-PEG synthesized powder, the sample T-450. The second phenomena observed in the presented results is the specific effect of lanthanum and its inhibition of crystallite growth and stabilization of the anatase phase, the samples TL-450 and TLP-450, Table 2. It is rather difficult for La^{3+} to replace Ti^{4+}

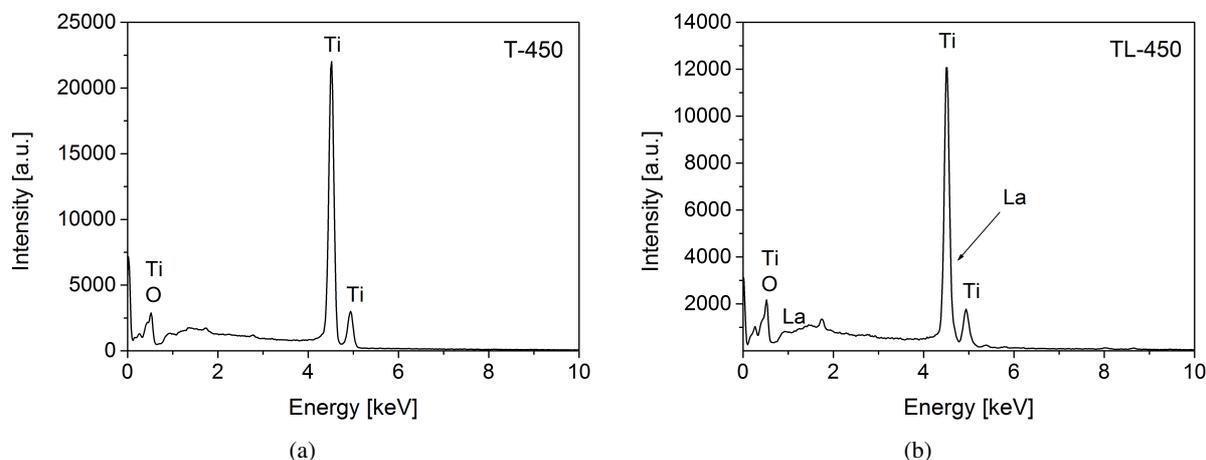


Figure 5. EDS spectra of titania nanopowders calcined at 450 °C : a) T-450 and b) TL-450

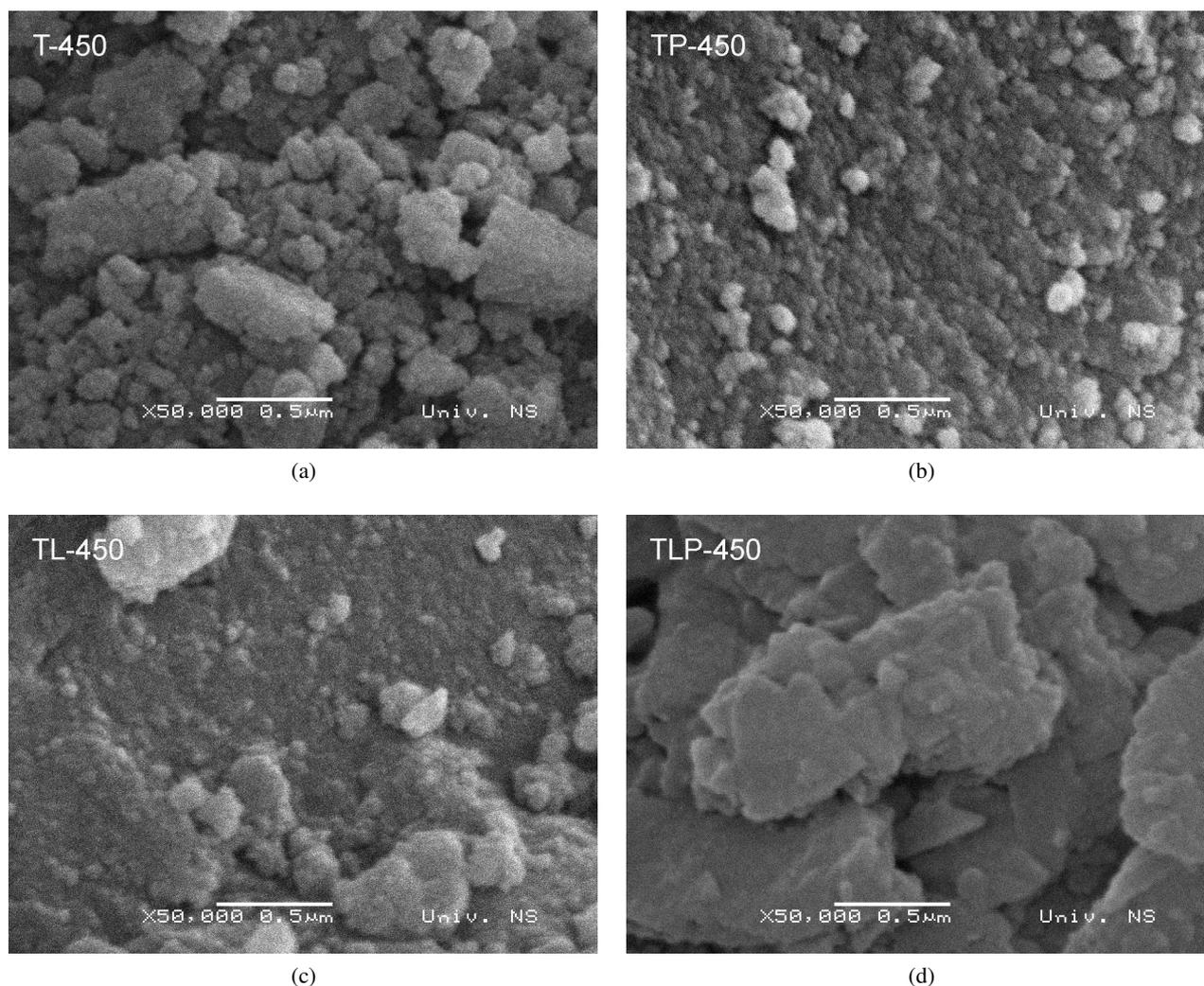


Figure 6. SEM images of titania nanopowders calcined at 450 °C: a) T-450, b) TP-450, c) TL-450 and d) TLP-450

inside the lattice, because the La^{3+} ionic size is much larger than Ti^{4+} one. However, it is believed that La incorporates into titania at low temperatures by the formation of Ti–O–La bonds on the surface of small particles [20]. This inhibits the movement of surface Ti atoms and particle coarsening by restricting direct contact of neighbouring crystallites, leading to the stabilization of the small anatase particles [21]. The average anatase particles size in titania powders without La^{3+} addition are in the range 10.6–16.3 nm (the samples T-450 and TP-450), in contrast to the powders with La^{3+} ions where the average anatase particle sizes are 4.1–6.1 nm (the samples TL-450 and TLP-450). The presented results indicate that La^{3+} as a dopant is efficient in hindering the crystallite growth and stabilization of anatase phase.

The presence of the lanthanum in the prepared nanopowders was confirmed by the energy dispersive X-ray spectroscopy, Fig. 5. According to the EDX patterns of the pure and La-doped titania, T-450 and TL-450 samples, it could be noticed that lanthanum is incorporated into titania doped nanoparticles.

Figure 6 shows the SEM micrographs of the titania nanopowders calcined at 450 °C for 5 h. The obtained powders consist of very fine primary particles which have a strong tendency to form agglomerates. The degree of agglomeration depends on the process parameters, such as the presence of PEG and La^{3+} ions. Agglomerates become more compact with the addition of PEG. This can be explained by assuming that during the agglomeration process, PEG adsorbs on the surface of TiO_2 particles producing coarsening and formation of compact agglomerates [22]. This can explain the particle growth in PEG treated samples. In the samples with La^{3+} ions, the effect of inhibiting the anatase crystallite growth is very noticeable in comparison to the undoped nanopowders. These findings are in accordance with the XRD results.

The pore size distributions and the N_2 adsorption-desorption isotherms of the titania nanopowders calcined at 450 °C are given in Fig. 7. All the samples show a typical IV isotherm with inflection of nitrogen-adsorbed volume at $P/P_0 = 0.4$ (type H2 hysteresis loop), indicating the presence of well-developed meso-

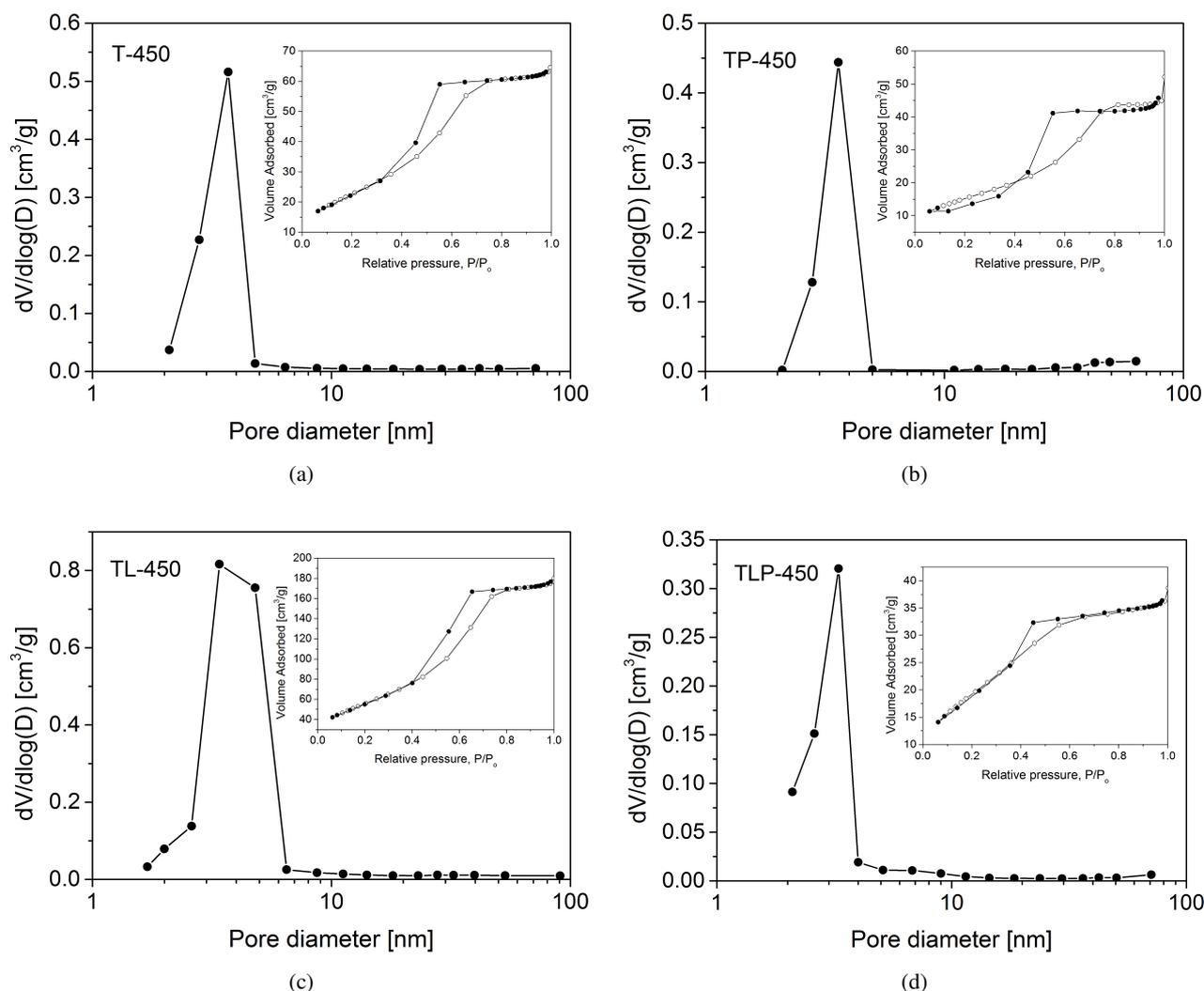


Figure 7. BJH pore size distributions curves and N_2 adsorption/desorption isotherms of titania nanopowders calcined at 450 °C: a) T-450, b) TP-450, c) TL-450 and d) TLP-450

porosity in the samples. The pore size distributions obtained from the desorption branch of the isotherms reveal the monomodal distribution of the pore sizes in the mesoporous region. The average pore diameters of the nanopowders are in the range 3.1–3.8 nm, Table 3. In addition, the mesopore size distribution for these nanopowders is narrow indicating a very good homogeneity of the pores. The steepness of the isotherms'

Table 3. Structural characteristics of titania nanopowders calcined at 450 °C

Sample	BET surface area [m ² /g]	Pore volume ^a [cm ³ /g]	Average pore diameter ^b [nm]
T-450	83.34	0.098	3.7
TP-450	55.64	0.069	3.4
TL-450	203.36	0.273	3.8
TLP-450	71.26	0.056	3.1

^aTotal pore volume calculated at $P/P_0 = 0.99$

^bEstimated using the desorption branch of the isotherm by the BJH method

desorption branch verifies the uniformity of the pore sizes. These results elucidate a good quality of the synthesized nanocrystals investigated in the present work. The highest BET surface area has the titania nanopowder doped with lanthanum, TL-450, around 203 m²/g. The severely increase of the surface area in comparison to the undoped titania nanopowder (T-450) is probably caused by the size of primary crystallites as well as the different phase composition of these samples. The relative high surface area of the doped sample confirms that the frameworks of mesoporous TiO₂ have better thermal stabilities. It should be noted that the presence of the PEG strongly affects the surface area and mesopore size, especially in the doped nanopowder. The addition of PEG induced a marked decrease in the specific surface area. This may be because the mesopore structure collapses during the removal of structure directing agent from the pores through the calcination step, which leads to a decrease in BET surface area, and an increase in particle size [23,24]. However, even then, these modified titania nanomaterials

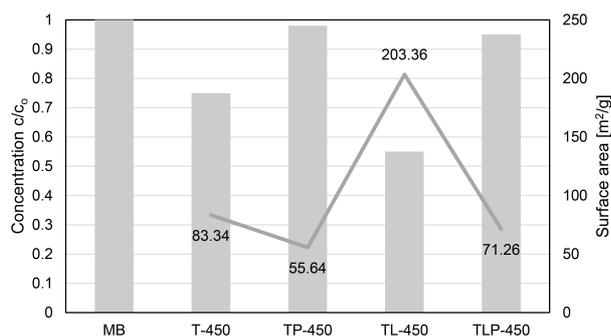


Figure 8. Photocatalytic degradation of MB by the modified titania nanopowders under UV light (material dosage = 2 g/L, solution volume = 50 mL, MB concentration = 40 mg/L, pH = 7, temperature = 25 °C; c_0 = concentration of solution after mixing in dark)

retained their mesoscale order at 450 °C with the predominantly crystalline anatase phase. This mesoporous structure could be a very promising as photoactive material for catalyst and other applications. Indeed, the preliminary studies of photocatalytic activity of the modified titania nanopowders were promising. The photocatalytic activity was evaluated by degradation of methylene blue (MB) dye under UV light irradiation. The blank experiments of MB degradation without catalyst under the same condition are compared. As expected, the nanopowder with the highest surface area, TL-450 has shown the highest photocatalytic efficiency. Figure 8 shows the photodegradation of MB by the modified titania nanopowders under UV light irradiation for 150 min. There is an obvious connection between the surface area and the efficiency of catalysts, i.e. the higher specific surface area the more efficient is the catalyst.

IV. Conclusions

Modified titania nanopowders (pure and La-doped) were prepared through a sol-gel method at the room temperature using a PEG template. It was found that the modification of nanocrystalline titania in the form of doping with lanthanum has a more positive effect than modification through PEG template. Namely, the incorporation of lanthanum could stabilize the anatase phase and increase substantially the surface area. The stabilization of the crystalline phase can be attributed to the more complete condensation between Ti–OH bonds and the inhibition of crystalline particle growth during the calcination. The addition of PEG during the synthesis favours the formation of anatase nanocrystals but also leads to the particle growth, which results in a decrease of the surface area. All the obtained powders consist of very fine primary particles with the sizes 4–6 nm in the non-PEG treated TiO₂ and 10–16 nm in the PEG treated TiO₂. After thermal treatment at 450 °C, anatase is a predominant phase in the undoped powders, while in the La-doped titania powders anatase is the only phase. In addition, the integrity of mesoporosity during calcination is preserved and all the nanopowders have the

mesoporous structure with the uniform and monomodal pore distribution with the pores of about 3 nm. These results indicate on a good quality of the synthesized nanocrystals which opens up the possibility to use the obtained titania nanomaterials in photonic applications. Investigations of photocatalytic activity have shown that the powder with the highest value of specific surface area is the most effective for MB removal.

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