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Photocatalytic bleaching of two organic dyes catalysed by La-doped nanosized TiO_2

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The aim of the present investigation is to synthesize and characterize pure and La-doped TiO_2 and to test as-prepared samples for photocatalytic activity. Doped and undoped samples were prepared by non-hydrolytic sol-gel method from titanium(IV) chloride, benzyl alcohol, and lanthanum(III) nitrate followed by thermal treatment. Lanthanum content in synthesized samples ranged from 0.4 to 5 mol.%. Structure and morphology of the obtained nanopowders were characterized by XRD, IR, and UV-Vis analysis. Average particle sizes of pure and doped TiO_2 were about 6–15 nm and anatase was found to be a dominant crystalline phase in the samples. It was estimated that particle sizes decreased on increasing La content.

The photocatalytic activity of titania samples for degradation of two organic dyes with different chromophores, triphenylmethane dye Malachite Green and xanthene dye Rhodamine B, was studied under UV and visible illumination. Addition of small amounts of La (0.4 and 1 mol.%) to TiO_2 was favourable for the photocatalytic activity under UV irradiation, while doping with 5 mol.% La led to a slower decolouration irrespective of used dye.

Keywords: La-doped titanium dioxide, sol-gel, photocatalytic activity.

INTRODUCTION

Titanium dioxide is one of the most investigated semiconductor photocatalysts for its long-term stability, non-toxicity, and excellent photocatalytic properties. It has been used to solve many environmental problems such as pollution of water, air, and soil. However, titania application is yet limited due to a fast recombination of electron-hole pairs and a large band gap, which corresponds with UV light. Modification of TiO_2 by doping with rare earth metals is a promising approach to improving its photocatalytic performance. Rare earth ion radii are larger than that of Ti^{4+}, so they can be distributed mainly on the surface of titania [1]. It is reported that lanthanide ions are able to form complexes with various organic compounds by interaction of their functional groups with lanthanide f-orbitals [2]. Thus, it is expected that organic pollutants could concentrate at the semiconductor surface, which may lead to enhancement of photocatalytic activity.

An enhanced photocatalytic activity was reported for rare earth doped TiO_2 under UV and visible light irradiation in several publications [3–8]. Among the various lanthanide metals examined, La, Ce, Eu, and Gd ions have been used widely [9].

It is well known that the effect of ion doping is strongly dependent on many factors, such as preparation route, doping method, dopant concentration, etc. For modifying TiO_2 with rare earth elements different techniques have been used: sol-gel technology, hydrothermal method, anodic oxidation, magnetron sputtering, electrospinning, co-precipitation, complexation, etc. [6, 10–17]. Sol-gel procedures are the most popular synthetic methods, which enable researchers to achieve superior compositional product homogeneity at moderate temperatures [15–17]. Among them, due to a slower reaction rate, non-hydrolytic sol-gel syntheses performed in organic solvents allow for better control over particle size and crystallinity degree [16–17].

This paper is a continuation of our previous research on preparation and properties of pure and modified nanosized TiO_2 catalysts by non-hydrolytic sol-gel method [18–25]. In the present work we report on the synthesis, characterization, and photocatalytic properties of La-doped TiO_2 derived by non-hydrolytic sol-gel procedure from titanium(IV) chloride, benzyl alcohol, and lanthanum(III) nitrate, the latter being a rare earth element source. Lanthanum content in the synthesized samples ranged from 0.4 to 5 mol.%. Photocatalytic activities of the synthesized powders were evaluated by degradation of two model organic pollutants under UV-Vis illumination: xanthene dye Rhodamine B (RhB) and triphenylmethane dye Malachite Green (MG). RhB is one of the most

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commonly used dyes in textile and paper industry. This dye is now banned from use in foods and cosmetics because it has been found to be potentially toxic and carcinogenic [28,29]. The triphenylmethane dye MG is widely used in aquaculture as a parasiticide and in food, health, textile and other industries. However, it has been reported that this dye can have carcinogenic, genotoxic, and mutagenic effects on fish, mammals, and other animals. Despite being banned in several countries, it is still being used in many parts of the world and poses risks for human health [30]. Therefore, photodegradation of these dyes is important with regard to the environmental cleanup.

EXPERIMENTAL

Preparation and characterization of titania catalysts

The starting materials in this study were titanium tetrachloride (≥99.0%, Fluka) used as a titania precursor, benzyl alcohol (≥99.5%, Merck), lanthanum(III) nitrate (Aldrich) as a rare earth element source, and absolute ethanol and diethyl ether from Merck. The Rhodamine B dye ($C_{28}H_{31}ClN_2O_3$) was purchased from Fluka while Malachite Green oxalate ($C_{46}H_{50}N_4.3C_2H_2O_4$) was supplied by Sigma. All the chemicals were used without further purification.

Pure and La-doped TiO_2 samples were prepared by means of non-hydrolytic sol-gel method based on the reaction between benzyl alcohol and titanium tetrachloride [26]. The main stages of sol-gel synthesis of lanthanum-modified titania samples are shown in figure 1. The reactions were performed in a regular glass beaker under controlled heating. For the preparation of La-modified titania, initially a proper amount of lanthanum(III) nitrate was dissolved in ethanol and mixed with benzyl alcohol. Then, titanium tetrachloride was slowly added to the beaker with benzyl alcohol at a volume ratio of 1:20 and the resulting sols were heated at 150°C under vigorous stirring for 10 h. Reaction mixtures were left for aging at room temperature for 10–14 days. Obtained white thick suspensions were centrifuged at 5000 rpm for 15 min and the supernatant was discarded by decantation. The precipitates were then washed twice with diethyl ether. After every washing step, the solvent was separated by centrifugation. The collected material was dried in air overnight and then ground into a fine powder. The obtained powders were calcined at 500°C for 2 h. In this way three modified xLa/TiO_2 samples were prepared: 0.4La/TiO_2, 1La/TiO_2, and 5La/TiO_2, where x represents La content as mol.%. Pure TiO_2 was prepared by the same procedure; however, lanthanum solution was replaced by anhydrous ethanol.

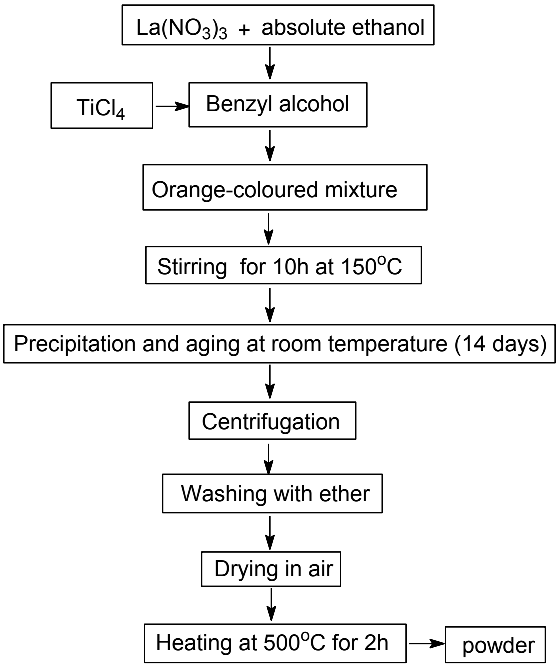


Fig. 1. Scheme of non-hydrolytic synthesis of La-doped TiO_2.

The structure and morphology of the resulting powders were characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray instrument), infrared (IR) spectroscopy using the KBr pellet method (Nicolet-320, FTIR spectrometer with a resolution of ±1 cm^{-1}, by collecting 64 scans in the range 1000–400 cm^{-1}), and UV-Vis spectroscopy (Spectrophotometer Evolution 300). Absorption edge and optical band gap were determined following instructions of Dharma et al. [27]. Bandgap energies of the samples were calculated by Planck's equation: $E_g = hc/\lambda = 1240/\lambda$, where E_g is bandgap energy (eV), h is Planck constant, c is light velocity (m s^{-1}), and λ is the wavelength (nm) (Table 1).

Table 1. Cut-off and optical band gap values for obtained compositions

Sample	Cut-off, nm	*Eg*, eV
undoped TiO_2	388.33	3.19
0.4% La-TiO_2	368.61	3.36
1% La-TiO_2	364.87	3.39
5% La-TiO_2	369.67	3.35

Photocatalytic activity procedure

The initial concentration of the RhB and MG aqueous solutions was 5 and 10 mg l^{-1}, respectively. In a typical procedure, a titanium sample (100 mg) was added to a 150-ml dye solution to form suspension. Prior to irradiation, the suspension was magnetically stirred for 30 min in the dark to reach an adsorption-desorption equilibrium of organic pollutant on the photocatalyst surface. A black light blue lamp (Sylvania BLB 50 Hz 8W T5) was used as a UV radiation source with a peak at 365 nm, and a 500-W halogen lamp (Sylvania) was used as the visible light source. In experiments, UV and visible light lamps were fixed above the treated solution at 10 and 40 cm, respectively. Blank tests were performed with dye solutions without catalysts in order to estimate possibilities for direct photolysis of the dyes.

All photocatalytic tests were performed under magnetic stirring (450 rpm) at a room temperature of 25°C. Aliquot samples of 3 ml were taken out at a regular time intervals from test solutions, centrifuged for 15 min at 5500 rpm, and filtered to remove catalyst particles. The photocatalytic degradation was monitored by measuring the absorbance of clear aliquots on a Jenway 6505 UV-Vis spectrophotometer at the characteristic wavelengths of the dyes: 555 and 618 nm for RhB and MG, respectively. Decolouration efficiency, *DE*, of the photocatalysts was calculated from equation (1):

$$DE = [(A_0–A_t)/A_0]\times 100\ , \qquad (1)$$

where A_0 is the absorbance at zero time and A_t is the absorbance at time t.

RESULTS AND DISCUSSION

Characterization of titania samples

XRD patterns of La-doped TiO_2 are shown in figure 2. As is seen, anatase (TiO_2) (JCPDS 78-2486) is a dominating crystalline phase detected by XRD. No peaks of rutile were observed. Moreover, lanthanum was not observed in the patterns, either. This indicated that La^{3+} ions were not incorporated into the TiO_2 crystal lattice to replace Ti^{4+}. Obviously, modification by lanthanum cannot enhance a phase transformation of anatase to rutile. Recently, it has been reported that La^{3+} dopant could inhibit the A-R phase transportation at high La^{3+}concentrations (above 2 at.%) [31]. In our previous investigations, it was established that Fe and N co-doping enhanced rutile crystallization which appeared at lower temperatures (500°C) [32]. Thus, it could be concluded that the doping effect of metal ions on A-R phase transformation is dependent on the physicochemical properties of doping metal ion as well as on its concentration. Average particle sizes of the as-synthesized La-doped TiO_2 samples calculated from diffraction line broadening using Scherrer equation were about 6–15 nm. It was estimated that particle sizes decreased on increasing La content (Fig. 2). For comparison, the particle size of pure TiO_2 obtained by non-hydrolytic sol-gel method is ~20 nm and these results are published elsewhere [22]. Probably, this is due to the nature of used precursors, experimental conditions as well as to applied non-hydrolytic sol-gel synthesis method [31, 33]. Our results of La-doped TiO_2 phase formation are in good agreement with those reported by other authors [31, 33].

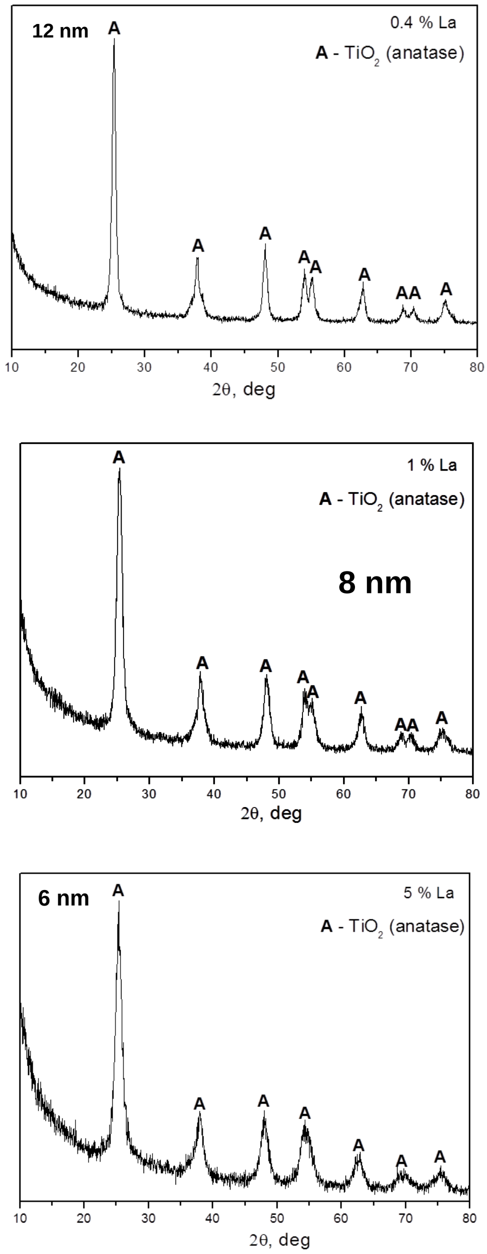


Fig. 2. XRD patterns of La-doped TiO_2.

The La-TiO_2 powders were investigated by means of IR spectroscopy in the range of 1000–400 cm^{-1} (Fig. 3a) where stretching vibrations of the inorganic building units are active. Generally, bands in the range of 600–400 cm^{-1} were observed that could be related to vibrations of TiO_6 building units

[23, 34]. No band shifts were observed upon increasing La content.

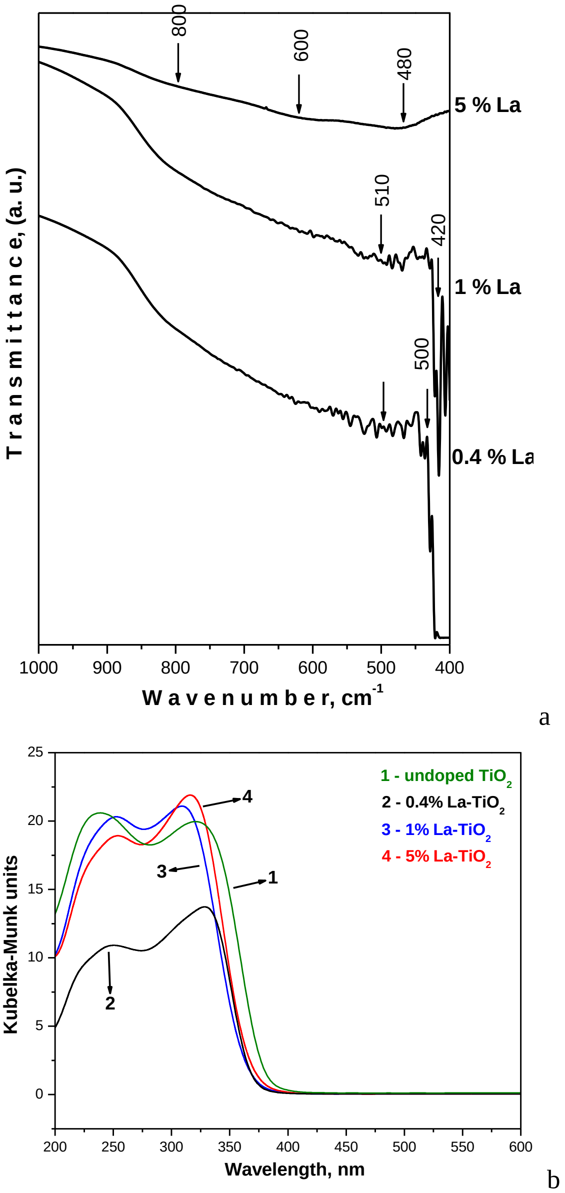


Fig. 3. (a) IR and (b) UV-Vis spectra of La-doped TiO_2.

UV-Vis diffuse reflectance spectra of La-modified and non-modified TiO_2 samples are shown in figure 3b. Registered absorption edges and calculated band gap values are given in Table 2. The observed absorption edge of the as-prepared samples varies in the region of 364–369 nm. The UV-Vis spectra of the La-doped TiO_2 samples display a shift of the absorption edge (~20 nm) in comparison with that of undoped TiO_2. According to Wang et al. [31] the blue shift is attributed to a quantum size effect. Evidently, the La^{3+} dopant did not cause any spectral changes. Our blue shifting results of the absorption edge are consistent with reference data [31].

Photocatalytic activity

A photocatalytic bleaching effect on the examined dyes was observed during all experiments with synthesized titania samples showing thereby that all these samples have exhibited some photo-activity. The photolysis of both dyes could be neglected, as after 180 min illumination in blank experiments less than 6% and 4% were removed under UV and Vis irradiation, respectively.

The photocatalytic performance varied with dopant content, type of irradiation, and type of model contaminant. Addition of small amounts of La (0.4 and 1 mol.%) to titania was favourable for the photocatalytic activity under UV irradiation, while doping with 5 mol.% La led to a slower decolouration irrespective of used dye (Figs. 4 and 5). Doping with 0.4 and 1 mol.% La improved the photoactivity under visible light illumination toward RhB (Fig. 4) and did not change it toward MG (Fig. 5).

According to many works [35–40], the photo-catalytic degradation rate can be described by assuming a pseudo-first order kinetic model (Eq. 2):

$$\ln C_0/C = kt\,, \qquad (2)$$

where C_o is the initial concentration and C is the concentration at any time, t. Semi-logarithmic plots of the concentration data gave straight lines and yielding rate constants from their slopes (Table 2).

Table 2. Rate constants (*k*) and decolouration efficiency (DE at 120 min) for dye photodestruction in presence of pure and La-doped TiO_2

Catalyst sample	UV illumination				Vis illumination			
	RhB		MG		RhB		MG	
	$k\times10^2$ min^{-1}	*DE*, %	$k\times10^2$ min^{-1}	*DE*, %	$k\times10^2$ min^{-1}	*DE*, %	$k\times10^2$ min^{-1}	*DE*, %
TiO_2	1.70	86	1.77	88	0.58	50	0.50	46
$0.4La/TiO_2$	2.10	76	2.49	95	1.05	69	0.32	31
$1La/TiO_2$	3.17	97	1.78	90	1.01	71	0.13	13
$5La/TiO_2$	2.10	93	0.86	65	0.54	47	0.01	3

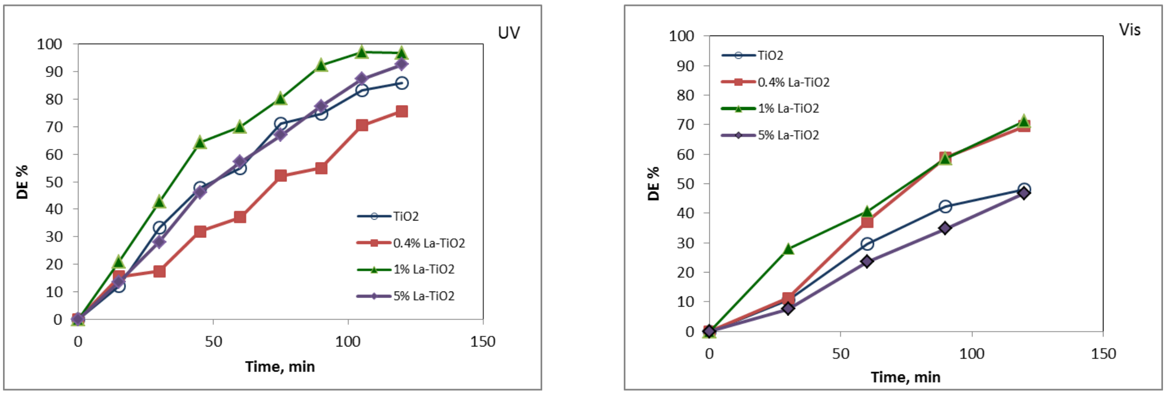


Fig. 4. Photocatalytic activity of La-modified samples against RhB under UV and Vis irradiation.

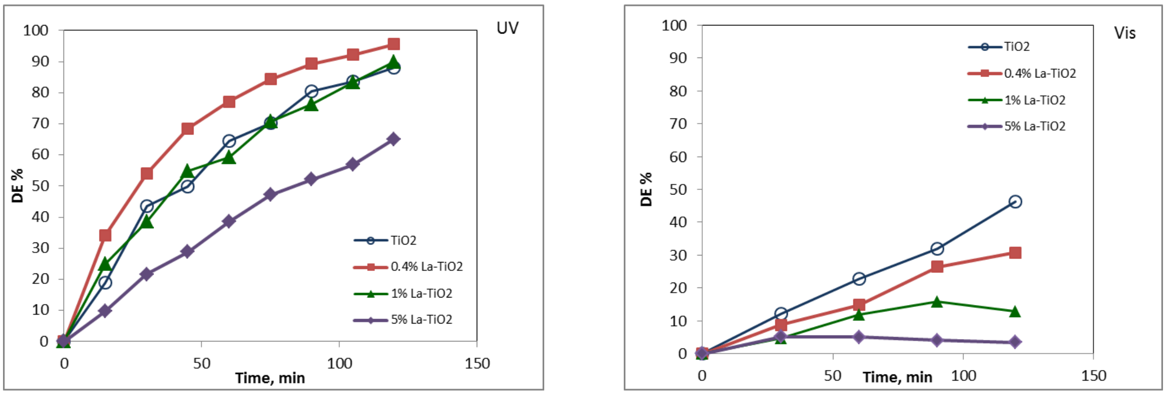
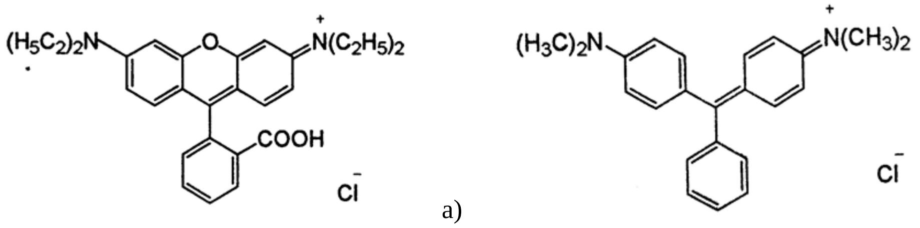


Fig. 5. Photocatalytic activity of La-modified samples against MG under UV and Vis irradiation.



a) b)

Fig. 6. Structure of model pollutants: a) Rhodamine B, b) Malachite Green

Our results confirm that the amount of dopant plays a significant role in affecting photo-degradation activity and an optimal concentration of dopant should be determined. Titania samples, modified with small amounts of La, exhibited good photocatalytic efficiency probably due to the effect of dopant ions as electron and hole trappers, which leads to suppression of electron-hole recombination and thus stimulating photocatalytic activity. However, surplus doped ions could serve as recombination sites by promoting charge-carrier recombination and doping can become detrimental [9]. Obviously, applying a non-hydrolytic sol-gel procedure and calcination temperature in the present study ensures an optimum doping amount within 0.4–1.0 mol.%, which agrees very well with that reported in the literature [41, 42]. According to some authors, the presence of La ions in the titania can affect the photocatalytic activity by creating oxygen vacancies and separating charge carriers [43].

In this study, photocatalytic process efficiency was determined not only by the type of titania catalyst and type of irradiation, but also by the chemical structure of the dyes. As can be seen in Figs. 4 and 5 and Table 2, RhB bleaching was faster than that of MG. This can be explained by the structure of the organic pollutants: RhB contains a heterocyclic ring, which is more vulnerable to splitting (Fig. 6).

CONCLUSIONS

Pure and doped titania nanopowders (6–12 nm) with different amount of La were synthesized by a non-hydrolytic sol-gel route. According to XRD patterns, mainly titania (anatase) was crystallized.

Particle sizes decreased on increasing lanthanum content. Addition of small amounts of La (0.4–1 mol.%) to titania was favourable for the photocatalytic activity under UV irradiation, while doping with 5 mol.% La led to a slower decolouration irrespective of used dye. Doping with 0.4 and 1 mol.% La improved the photoactivity under visible light illumination toward RhB and did not change it toward MG.

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ФОТОКАТАЛИТИЧНО ОБЕЗЦВЕТЯВАНЕ НА ДВЕ ОРГАНИЧНИ БАГРИЛА КАТАЛИЗИРАНО ОТ НАНОРАЗМЕРЕН TiO_2 ДОТИРАН С ЛАНТАН

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(Резюме)

Целта на настоящото изследване е да се синтезират и охарактеризират чист и дотирани с лантан TiO_2 образци и да се изследват фотокаталитичните им свойства. Дотирани и недотирани образци бяха получени чрез нехидролитичен зол-гел метод от титанов(IV) хлорид, бензилов алкохол и лантанов(III) нитрат, с последваща термична обработка. Съдържанието на лантан в образците варира от 0.4 до 5 мол.%. Структурата и морфологията на получените нанопрахове са охарактеризирани чрез РФА, ИЧ и УВ-видима спектроскопия. Относителният размер на частиците на чистия и дотирания TiO_2 е около 6–15 nm и доминиращата кристална фаза в получените образци е анатаз. Установено е, че размерът на частиците намалява с повишаване на съдържанието на лантан.

Фотокаталитичната активност на TiO_2 за разграждане на две органични багрила с различни хромофори – трифенилметановото багрило (Малахитово зелено) и ксантеновото багрило (Родамин Б) беше изследвана при облъчване с ултравиолетова и видима светлина. Добавянето на малко количество лантан (0.4 и 1 мол.%) благоприятства фотокаталитичната активност при облъчване с УВ, докато дотирането с 5 мол.% лантан води до по-бавно обезцветяване, независимо от вида на използваното багрило.