

NEW DEVELOPED (Ag)-La₂O₃-Ce₄O₇-ZnO
PHOTOCATALYTIC ACTIVE COMPOSITES
FOR TEXTILE DYES DEGRADATION

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Abstract

New La₂O₃-Ce₄O₇-ZnO photocatalytic active composites were synthesized using Pluronic-assisted co-precipitation route, followed by calcination at 450 °C. The silver doping of the prepared La₂O₃-Ce₄O₇-ZnO material was performed by impregnation with aqueous solution of AgNO₃. The average crystallites size 3 nm and 39 nm for Ce₄O₇ and ZnO phases were estimated by PXRD analysis. The XPS study determined that the La3d_{5/2} peak is positioned at 834.1 eV and corresponds to La₂O₃. The binding energy of the Ag3d_{5/2} peak of the Ag-La₂O₃-Ce₄O₇-ZnO powder is at 367.2 eV and the amount of the silver on the surface is 0.8 at.%. The obtained values of the modified Auger zinc and silver parameter are 2010.5 eV and 724.4 eV and correspond to Zn²⁺ and Ag²⁺ oxidation states, respectively. The silver doping enhances the photocatalytic efficiency of La₂O₃-Ce₄O₇-ZnO sample for degradation of Reactive Black 5 dye (78%) at 150 min UV irradiation compared to that of the undoped sample (52%). The undoped sample demonstrates the higher photocatalytic ability for degradation of Malachite Green dye (degree of degradation at 150 min – 80%) in comparison with Reactive Black 5 dye (52%).

Key words: silver doped La₂O₃-Ce₄O₇-ZnO, photocatalyst, Malachite Green dye, Reactive Black 5

Introduction. The discharged wastewater by dyeing and textile industries seriously influences the environment and life of people. The polluted coloured

waters from textile industry block the sunlight which is important for various photochemical reactions in aquatic systems. Contamination of natural water is often due to the fact that the used dyes are released directly in aqueous systems. It is very important to remove dyes from wastewater before it is discharged into the environment. The toxicity of these organic contaminants causes a damage to microorganisms, aquatic life and people. Thus the removal of dyes contained in industrial wastewater has attracted the attention) [1]. Photocatalytic degradation of organic pollutants using semiconductor material catalysts has been known as a promising method for water treatment because it is cheap, environment-friendly, effective, and able to utilize directly the solar energy [2]. In the literature has been discussed the preparation and photocatalytic behaviour of binary composites $\text{CeO}_2\text{-ZnO}$ [3, 4], $\text{CeO}_2\text{-CuO}$ [5], $\text{CeO}_2\text{-Sm}_2\text{O}_3$ [6], $\text{La}_2\text{O}_3\text{-ZnO}$ [7]. The $\text{ZnO-CeO}_2\text{-TiO}_2$ composite oxide was synthesized by the combustion method and possesses better photocatalytic properties about decolourizing of Methylene Blue dye [8]. PRABHU et al. [9] have obtained $\text{ZnO-CeO}_2\text{-TiO}_2$ with enhanced photocatalytic ability about Rhodamine B dye using sol-gel method. The $\text{Ag}_2\text{O-CeO}_2\text{-ZnO}$ nanocomposites prepared by co-precipitation method following calcination possess excellent photocatalytic ability toward Methyl Violet 6b dye [10]. There are scarce data in the literature about tricomponent composites combining ZnO , Ce_4O_7 and La_2O_3 oxides.

The aim of the present study is to check the photocatalytic efficiency towards photocatalytic UV degradation of model textile dyes of newly developed undoped and silver doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ composites.

Experimental. Preparation of undoped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ materials. The $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ sample was prepared using 0.09 M aqueous solutions of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Valerus Co.) and $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Alfa Aesar) mixed in ratio 1:1 at constant stirring for 10 min. The 2.5 g tri-block copolymer Pluronic P123 (Sigma-Aldrich, Mw = 5800) was dissolved in 50 ml distilled water at constant stirring for 1 h and added to the mixture of nitrate precursors. The obtained mixture from nitrate precursors and Pluronic P123 was stirred for 10 min. The precipitant 2M NaOH (Valerus Co.) was added drop by drop in the mixture of aqueous solutions of nitrate precursors and Pluronic P123 until pH reached 12 at continuous stirring. After co-precipitation the suspension was stirred for 10 min at room temperature and then 40 min at 45 °C. The precipitate was filtered and washed with distilled water several times. The obtained precipitate was dried at 35 °C and calcined at 500 °C for 3,5 h in air atmosphere. The sample was labeled **N1**. Then the material was impregnated with aqueous solution of AgNO_3 . After that the doped material was calcined at 450 °C for 3,5 h in air medium. The sample doped with 0.3 wt. % Ag was marked **N2**.

Physicochemical characterization. The Powder X-ray diffraction (PXRD) analyses were performed on Bruker D2 Phaser diffractometer within the range of 2θ values between 10° and 100° using Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm) at

40 kV. The presence of the phases in the prepared materials was determined by the ICDD database. The Debye–Scherrer equation

$$(1) \quad D = K \cdot \lambda / (\beta \cdot \cos \theta)$$

was used to calculate the crystallite sizes of the synthesized samples. Here D is the average crystallite size in angstroms, K is a constant, which is accepted to be 0.89, λ is the wavelength of the X-ray radiation (Cu $K\alpha$, 0.15406 nm), β is the corrected band broadening (FWHM) after subtraction of equipment broadening, and θ is the diffraction angle.

The surface composition and electronic structure were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on AXIS Supra electron-spectrometer (Kratos Analytical Ltd.) using achromatic Al $K\alpha$ radiation with a photon energy of 1486.6 eV and charge neutralisation system. The binding energies (BE) were determined with an accuracy of ± 0.1 eV. The chemical compositions in the depth of the films were determined monitoring the areas and binding energies of C1s, O1s, Zn2p, Ce3d, La3d and Ag3d photoelectron peaks. Using the commercial data-processing software of Kratos Analytical Ltd. the concentrations of the different chemical elements (in atomic %) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors.

FTIR investigations were carried out on a Bruker-Vector 22 apparatus in the range of 400–4000 cm^{-1} , using KBr pellets.

Photocatalytic tests. The investigations about photocatalytic degradation of Malachite Green (MG) and Reactive Black 5 (RB5) as model pollutants (5 mg/L aqueous solution of dyes), using undoped and doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ as photocatalysts under UV illumination were performed. Polychromatic UV-A lamp (Sylvania BLB, 18 W) with an emission maximum at 365 nm was used. The intensity of illumination is 0.66 mW/ cm^2 measured by Cole Parmer Radiometer VLX-3.W. The distance of illumination between lamp and photocatalytic reactor is 10 cm. The photocatalytic tests were carried out in semi-batch slurry reactor using 0.15 g photocatalyst and 150 ml of dye solution under constant stirring and air flowing. To reach adsorption-desorption equilibrium state the studied systems were left in the dark for about 30 min before switching on the UV irradiation for 2.5 h. The powder was separated from the aliquot solution by centrifugation. After that the change of absorbance during the photocatalytic tests was monitored by UV-Vis absorbance spectrophotometer UV-1600PC in the wavelength range from 200 to 800 nm ($\lambda_{\text{max}} = 618$ nm for MG and 598 nm for RB5). The degree of dye degradation was calculated using the dependence $((C_0 - C)/C_0) \times 100$, where C_0 and C were initial concentration before turning on the illumination and residual concentration of the dye solution after illumination for selected time interval.

Results and discussion. The Powder X-ray diffraction patterns of the two synthesized materials **N1** and **N2** are presented in Fig. 1A. The performed Powder

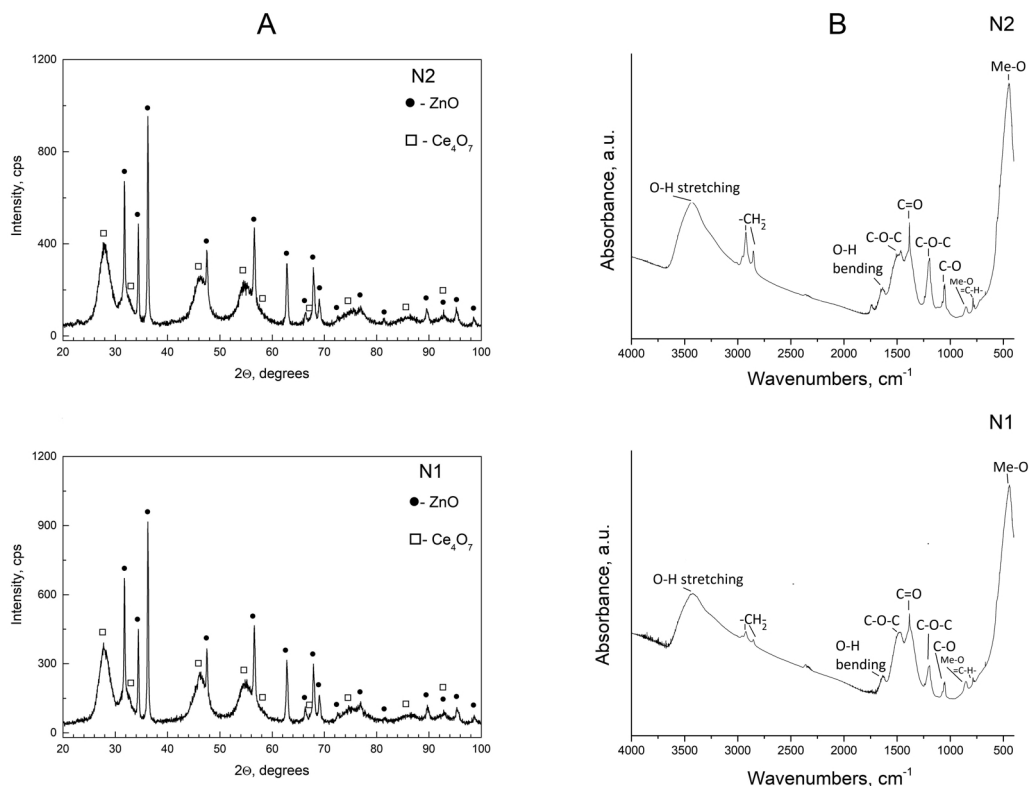


Fig. 1. A) PXRD patterns, and B) FTIR spectra of synthesized undoped and doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ powders

X-ray diffraction studies established the existence of Ce_4O_7 (PDF-657999) and ZnO (PDF-361451) phases in both samples. The determined mean crystallite size of Ce_4O_7 and ZnO phases in the undoped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ and doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ materials is 3 nm and 39 nm, respectively. The peak identifying the presence of La_2O_3 is not registered. The reason for this could be that La_2O_3 is highly dispersed in the synthesized materials or it is segregated as very small particles which are not detected using PXRD [11]. The silver phase has not been detected due to its small quantity below the sensitivity threshold.

The FTIR spectra of synthesized materials are displayed in Fig. 1B. The broad bands about 3422 cm^{-1} (sample N1) and 3433 cm^{-1} (sample N2) are due to the stretching vibration of the O-H bond of the physically adsorbed water molecule on the surface of catalysts. The characteristic peak observed at 1636 cm^{-1} is assigned to the OH bending vibration of the adsorbed water molecule. The peaks located in the region $443\text{--}850\text{ cm}^{-1}$ are assigned to the vibrations of Me-O (Me = La, Zn, Ce), respectively [12–14]. The bands observed in the range $2924\text{--}2852\text{ cm}^{-1}$ correspond to symmetric and asymmetric stretching vibrations of the aliphatic groups $(-\text{CH}_2)_n$ of the Pluronic P123. The peaks positioned at about

1384 cm⁻¹, 1195 cm⁻¹, 1507 cm⁻¹, and 785 cm⁻¹ are due to stretching vibration C = O, C–O–C and bending vibration = C–H- of Pluronic P123, respectively. The stretching vibrations of the C–O bond are registered at 1051 cm⁻¹. The presence of absorption bands of Pluronic P123 in the FTIR spectra of the undoped and silver doped La₂O₃-Ce₄O₇-ZnO materials after thermal treatment could be explained by the “delayed” decomposition of the polymer template, which is due to the interaction with mixed metal oxides [15].

The surface composition and chemical state of the undoped and doped La₂O₃-Ce₄O₇-ZnO powders were investigated by XPS. Photoelectron spectra of C, O, Zn, Ce, La and Ag are registered on the surface (Fig. 2). The quantities of the chemical elements observed on the surface are shown in Table 1.

T a b l e 1
XPS results of the concentrations of the chemical elements

Samples	O, at.%	Zn, at.%	Ce, at.%	La, at.%	Ag, at.%	Area O-Me/OH
N1	68.8	12.4	9.0	9.8	—	1.5
N2	71.0	12.1	7.3	8.8	0.8	1.1

The O1s peaks are wide and asymmetric and could be deconvoluted by Lorentzian–Gaussian curve fitting into two components. The first ones at ~ 539.7 eV are assigned to lattice oxygen in metal oxides and the second peaks at ~ 532.0 eV are attributed to hydroxyl groups, which are more in sample **N2** (Table 1).

The binding energy of the Ag3d_{5/2} peak of the La₂O₃-Ce₄O₇-ZnO powders doped with silver is at 367.2 eV and amount of the silver on the surface is 0.8 at.% (Fig. 2). It is also observed that the values of the binding energies are with small differences and it is not possible to distinguish the oxidation states of the silver. This requires the modified Auger silver parameter to be determined. The obtained value is 724.4 eV and according to literature data, corresponds to AgO [16]. The use of Auger parameter is more correct than the binding energy of Ag3d_{5/2}, due to Ag MNN auger transition showing a more remarkable chemical shift than photoelectron peaks.

The position of the Ce3d peaks indicates that cerium is in phase CeO₂ with binding energies at 882.1 eV for Ce3d_{5/2} but the shape indicates that there is a small amount of Ce³⁺ [17]. After calculation, it was found that for **N1** Ce³⁺ is 10.3%, and for **N2** it is 8.7%. The La3d peaks are positioned at 834.1 eV and correspond to La₂O₃.

Generally, the values of the binding energies of the registered Zn2p_{3/2} peaks are in the range 1021.6–1021.8 eV. These small differences in values do not make it possible to accurately determine the differences in the chemical states of Zn atoms. For a more accurate determination of the chemical state of zinc, the modified Auger parameter was used, which is the sum of the kinetic energy of the Auger

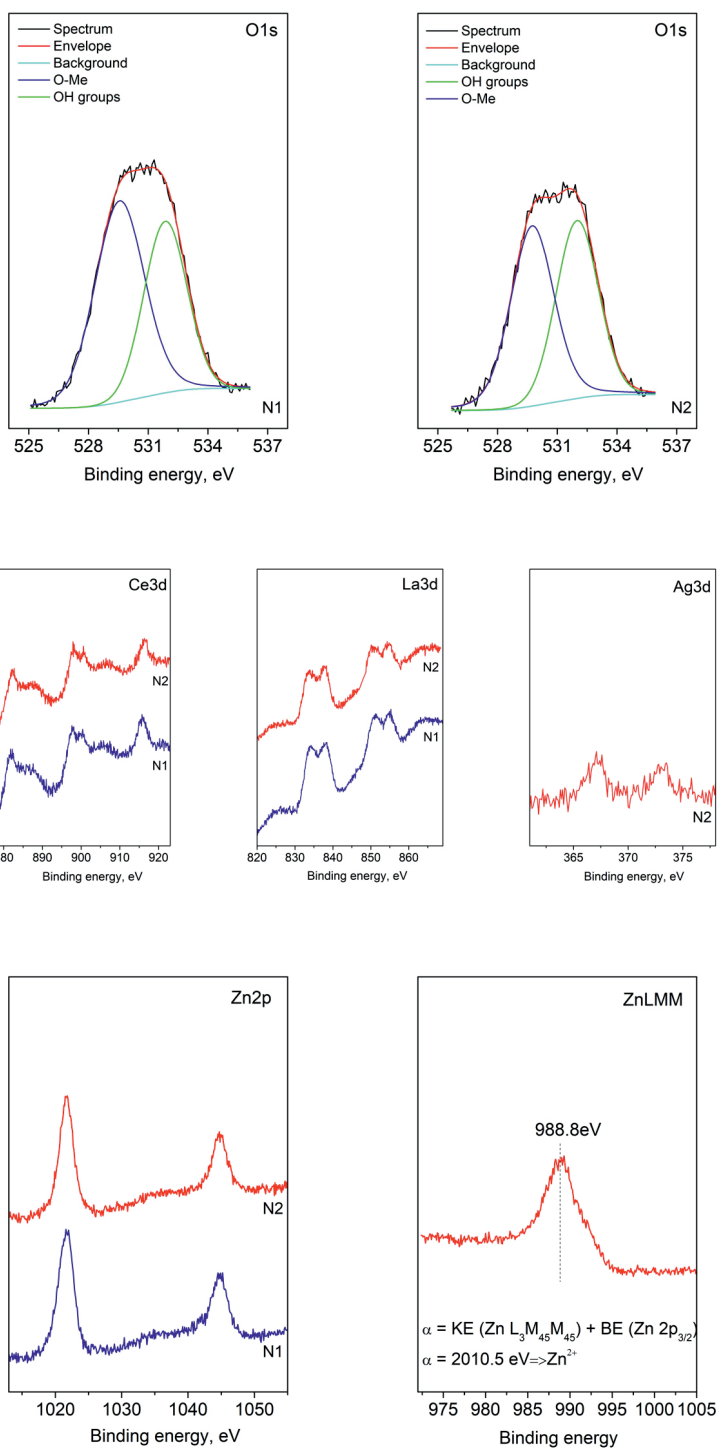


Fig. 2. Core level spectra of O1s, Ce3d, La3d and Ag3d of undoped and doped La_2O_3 - Ce_4O_7 -ZnO powders (N1 and N2)

transition Zn $L_3M_{45}M_{45}$ and the binding energy of the Zn $2p_{3/2}$ photoelectron peak:

$$(2) \quad \alpha = KE(\text{Zn } L_3M_{45}M_{45}) + BE(\text{Zn}2p_{3/2}).$$

It eliminates the influence of the electrostatic charge on the surface due to photoemission. The binding energy of the Zn $2p_{3/2}$ photoelectron peaks is 1021.7 eV. The obtained values of the Auger parameter are = 2010.5 eV (Fig. 2). According to literature data, the values of this parameter in the range 2009.5–2010.5 eV correspond to Zn $^{2+}$ oxidation state [18].

The photocatalytic degradation of two model pollutants MG and RB5 dyes in aqueous solutions under UV irradiation using the synthesized **N1** and **N2** photocatalysts was investigated. Figure 3 illustrates the concentration ratio C/C_0 and degree of degradation of MG and RB5 dyes as a function of the UV irradiation time. Sample **N1** demonstrates the higher photocatalytic ability for degradation of Malachite Green dye (degree of degradation at 150 min – 80%) in comparison with that towards Reactive Black 5 dye (52%). Silver doping enhances the photocatalytic efficiency of Ce-Zn-La oxide sample for degradation of Reactive Black 5 dye (78%) at 150 min UV irradiation compared to that over the undoped sample (52%). The silver doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ exhibits slightly higher degradation activity for MG dye in comparison with the undoped material but after 120 min irradiation the photocatalytic ability of Ag doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ slows down fast probably due to irreversible dye adsorption. The apparent rate constants of tested photocatalysts were calculated using logarithmic linear dependence $-\ln(C/C_0) = k \cdot t$ and followed the pseudo first-order kinetics. The value of apparent degradation rate constants of MG and RB5 dye using $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ and silver doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ photocatalysts are $13.2 \times 10^{-3} \text{ min}^{-1}$; $16.1 \times 10^{-3} \text{ min}^{-1}$ and $4.6 \times 10^{-3} \text{ min}^{-1}$; $8.1 \times 10^{-3} \text{ min}^{-1}$, respectively.

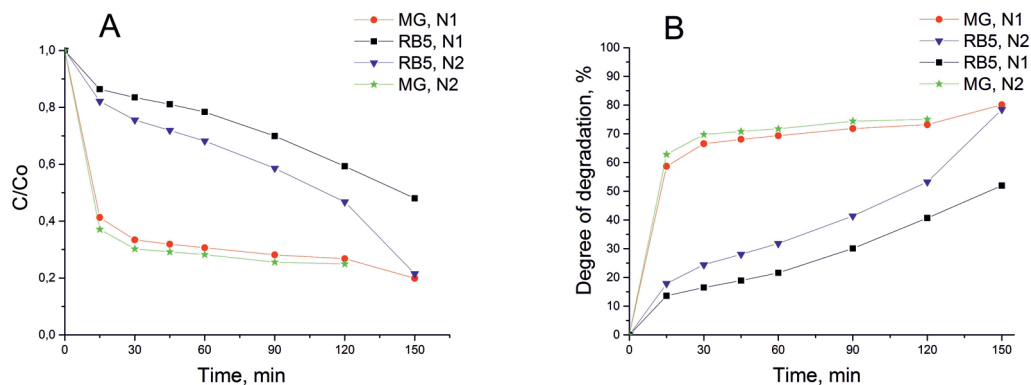


Fig. 3. A) Concentration ratio C/C_0 , and B) degree of degradation of MG and RB5 as a function of UV irradiation time using undoped and doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ photocatalysts

A positive influence could be ascribed to the presence of Ce^{3+} ions (proved by XRD and XPS analyses). They work as electronic capturing centres, thus leading to slower electron-hole pair recombination [19].

Another possible reason for the enhanced photocatalytic activity of silver doped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ material is the ability of silver to modify the interfacial charge transfer to electron acceptors such as oxygen and also its ability to trap electrons [20].

The combination of presence of Ce^{3+} and the effect of the doping with Ag leads to increased photocatalytic activity of (Ag)- $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ powders.

Conclusion. The newly obtained (Ag)- $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ photocatalysts was successfully prepared by pluronic-modified process. The silver doping of $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ materials improved their photocatalytic ability to degrade Reactive Black 5 dye as model pollutant. Undoped $\text{La}_2\text{O}_3\text{-Ce}_4\text{O}_7\text{-ZnO}$ photocatalysts exhibit higher photocatalytic activity to Malachite Green dye in comparison with that of Reactive Black 5 dye.

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