

# Synthesis, Characterization and Sonocatalytic Activity of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> Films for the Degradation of Organic Dyes

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## Abstract

The sonocatalytic degradation of organic dyes (C.I. 50040, C.I. Reactive Red 1, C.I. Acid Orange 7) catalysed by Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films was studied. For the preparation of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films, the sol-gel coating process was used. The phase composition, morphology, precursor at different temperatures and emitting light properties of the calcined powders were analysed by X-ray diffraction (XRD), absorption spectra and upconversion emission spectra. The X-ray diffraction of powder samples of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> took on anatase main peaks and upconversion luminous agent, respectively. Analysis of absorption spectra of amorphous Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> showed that doping N stretching vibration peak of water or hydroxyl adsorption, Co<sup>2+</sup> ion had very strong absorption in 1.0–1.7 μm wavelength range, the transition luminescence of Er<sup>3+</sup> ions was just on Co<sup>2+</sup> ions absorption band. The emission spectrum indicated that Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> could launch green 500–560 nm and red 650–700 nm, 525, 550 and 660 nm peaks corresponding to <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>H<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition of Er<sup>3+</sup>. Doping Co and N enhanced the upconversion luminescence and absorption effect. Sonocatalytic degradation effect of organic dyes loading Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> was better when ultrasonic intensity was equal to 15 W cm<sup>-2</sup>. The degradation ratios of aqueous solutions of these three kinds of organic dyes by ultrasonic irradiation were obviously lower than by ultrasonic irradiation together with Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films in the same conditions. Degradation kinetics of organic dyes by ultrasonic irradiation and by ultrasonic irradiation cooperating with Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films followed the first-order reaction.

## Key words

Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>, upconversion emission spectra, sonocatalytic, dye degradation

## Introduction

Recently, photocatalytic degradation of organic pollutants assisted by TiO<sub>2</sub> has been extensively investigated because of its strong oxidation ability, low energy consumption, and simple operation.<sup>1,2</sup> The discharge from the textile industries contains a lot of inorganic salts and surface-active agents. Inorganic salts and surfactants have complicated influence on the photocatalytic treatment processes of dye effluents.<sup>3</sup> The research of E. Y. Bae et al.<sup>4,5</sup> manifested that the ultrasonic mineralization aided efficiently in opaque or low transparent degradation of dye effluents. K. Okitsu et al.<sup>6,7</sup> reported ultrasonic and solar photocatalytic decomposition of organic dye in aqueous solution. Owing to broadband gap of TiO<sub>2</sub>, only a small fraction (ultraviolet light) of sonoluminescence could be taken advantage of in sonocatalytic degradation. According to J. Wang et al.<sup>8,9,10</sup> the upconversion luminescence agent could transform visible light into ultraviolet light, which might activate the TiO<sub>2</sub> efficiently. Moreover, some semiconductor materials uniting some upconversion luminescence agent may improve the catalytic degradation efficiency for further expanding the spectral response range of ultrasound catalysis.

The preparation of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and the characterization of XRD are presented. This study details the ef-

fects on crystal structure, spectra, degradation efficiency of organic dye in sonocatalytics of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>.

## Experimental

### Materials

Y<sub>2</sub>O<sub>3</sub> (purity 99 %), Er<sub>2</sub>O<sub>3</sub> (purity 99 %), CoO (purity of 99 %), HNO<sub>3</sub> (analytically pure) (Veking Company, China) and Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O were used to prepare Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>. Diethanolamine (C<sub>4</sub>H<sub>11</sub>NO<sub>2</sub>), tetrabutyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>6</sub>O), H<sub>2</sub>O, acetic acid (CH<sub>3</sub>COOH), and polyethylene glycol 3000 (HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H) were used to synthesize TiO<sub>2</sub> gel.

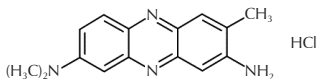
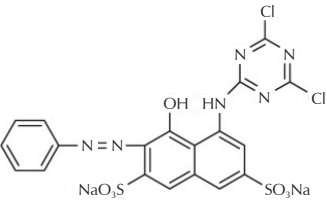
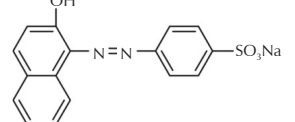
C.I. 50040 (C<sub>15</sub>H<sub>17</sub>ClN<sub>4</sub>), C.I. Reactive Red 1 (C<sub>19</sub>H<sub>10</sub>-Cl<sub>2</sub>N<sub>6</sub>O<sub>7</sub>S<sub>2</sub>Na<sub>2</sub>) and C.I. Acid Orange 7 (C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>NaO<sub>4</sub>S) (99.99 % purity) were obtained from Tianjin Kaiyuan Reagent Corporation (China). Their characteristics are listed in Table 1.

### Synthesis of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>

Y<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and CoO (the molar ratio of Er<sup>3+</sup> : Co<sup>2+</sup> : Y<sup>3+</sup> equal to 1 : 9 : 90) were dissolved in HNO<sub>3</sub>, and excess HNO<sub>3</sub> was evaporated to obtain the lanthanide nitrates. Second, Al(NO<sub>3</sub>)<sub>3</sub> (moles ratio of [Y(NO<sub>3</sub>)<sub>3</sub> + Er(NO<sub>3</sub>)<sub>3</sub>] and Al(NO<sub>3</sub>)<sub>3</sub> = 3 : 5) was added to the lanthanide nitrates, which were then *N,N*-dimethylformamide to produce Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> solution.

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Table 1 – Characteristics of organic dyes  
 Tablica 1 – Karakteristike organskih bojila

Dye Bojilo	Relative molecular mass Relativna molekulska masa	Maximum absorption wavelength, $\lambda_{\max}$ /nm Valna duljina maksimuma apsorpcije, $\lambda_{\max}$ /nm	Chemical structure Kemijska struktura
C.I. 50040	288.78	(50 % ethanol) 533	
C.I. Reactive Red 1	615.39	540	
C.I. Acid Orange 7	350.32	484	

In the preparation of composite  $\text{TiO}_2$  gel, the molar ratio of diethanolamine : tetrabutyl titanate : ethanol :  $\text{H}_2\text{O}$  : acetic acid : polyethylene glycol 3000 was equal to 2 : 1 : 20 : 2 : 0.3 : 0.002. First, tetrabutyl titanate and diethanolamine were added into ethanol and agitated for 1 hour with magnetic stirrer against white flocculent precipitation. Deionized water and acetic acid were then dripped in slowly and at the same time agitated for 10 minutes. Next, the above  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}$  solution was dripped in and stirred at the same time, after which polyethylene glycol 3000 was added, and stirred for another 3 hours. Finally,  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$  gel was prepared.

The glass slides were cleaned and dried with deionized water and ultrasonic wave.  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$  gels were sprayed on glass slides by ultrasonic spraying equipment (Beijing Dongfang Jinrong ultrasonic electric Co. Ltd.). Spraying width was 20 mm, the flow rate was  $10 \text{ ml min}^{-1}$ . After the wet films had dried, they were put into the heating furnace for heat treatment, with  $2 \text{ }^\circ\text{C min}^{-1}$  up to  $120 \text{ }^\circ\text{C}$ , with 120 min insulation, in order to strengthen the porous thin films of  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$ .

### Sonocatalytic degradation of the organic dye

The experimental apparatus is shown in Fig. 1. The reactor with a built-in trough was placed on a magnetic stirrer. The glass slides with  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$  thin films were inserted into the trough. The glass slides had tiny holes so that dye solutions could pass through them to distribute homogeneously in the degradation process. The ultrasonic probe (model of ultrasonic generator: 88-1, frequency: 22 kHz) was put into the reactor. The samples of three kinds of dye solutions (C.I. 50040, C.I. Reactive Red 1, C.I. Acid Orange 7) in the reactor were dispersed under ultrasonic irradiation for 120 minutes, while sampled once every 20 minutes, which immediately dispersed by centri-

fuging 15 minutes at  $6000 \text{ r min}^{-1}$ . Each test was repeated three times, and the averages of tests were taken.

The concentrations of the samples were measured by an Aquamate™ Plus UV-vis spectrophotometer (Thermo Scientific Company). The concentrations of C.I. 50040, C.I. Reactive Red 1, and C.I. Acid Orange 7 were determined at their respective maximum absorbance.

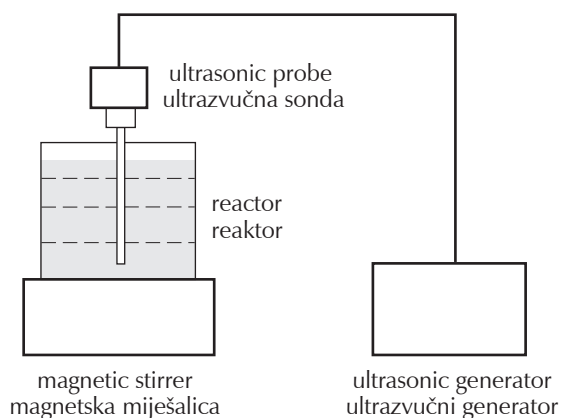


Fig. 1 – Schematic diagram of the experimental setup  
 Slika 1 – Shematski dijagram postavki eksperimenta

### Analytical method

The X-ray diffractometer (Model: D8 Advance) was used to characterize the samples of  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$  nanoparticles. The upconversion emission spectra of the samples were tested by Hitachi F-4500 fluorescence spectrometer. The UV/VIS/NIR spectrometer (Model: V-570JASCO) was used to analyse the absorption spectrum at ambient temperature. The absorbance of dye solution was determined by Shimadzu 2450 UV-vis spectrophotometer.

## Results and discussion

### Characterization

Firstly, Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> gels were heated to 90 °C for 1 hour, and then milled into fine powders. Second, they were put into the muffle furnace (Model: DC-B8/12) to calcine at 1160 °C for 2 hours, and then cooled to ambient temperature. Fig. 2 illustrates their X-ray diffraction pattern. The main characteristic diffraction peaks appeared at  $2\theta = 18.2^\circ, 25.6^\circ, 27.4^\circ, 29.8^\circ, 33.6^\circ, 41.1^\circ, 46.6^\circ,$  and  $55.1^\circ$ . Compared JCPDS card, they were the characteristic diffraction peaks of the anatase and the upconversion luminous agent, respectively. The characteristic diffraction peaks broadened owing to doping Co and N in Fig. 2.

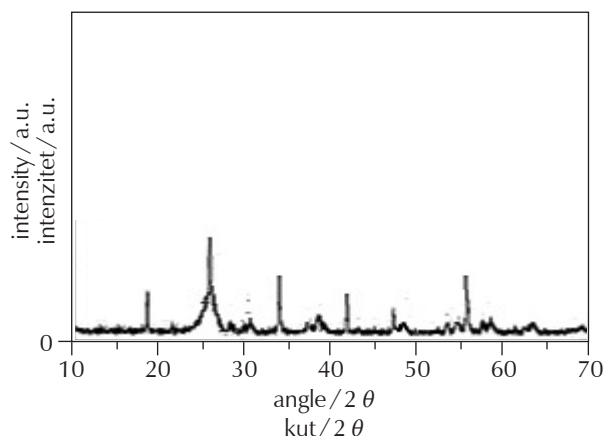


Fig. 2 – XRD pattern of the samples of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> nanoparticles

Slika 2 – XRD obrazac uzoraka nanočestica Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>

### Spectral characteristics

The absorption spectra of crystalline Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> is illustrated in Fig. 3. Doping N could broaden vibration peak of the adsorption of water or hydroxyl and Ti–O vibration peak that had been stretched and shifted to lower wavenumbers. Co<sup>2+</sup> ions had strong absorption band at 1.0 – 1.7 μm wavelength range, the transition luminescence of Er<sup>3+</sup> ions was just in Co<sup>2+</sup> ions absorption band. The absorption peak at 1.55 μm was just corresponding to <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub> (<sup>4</sup>F) energy level transition of Co<sup>2+</sup>. The absorption curve, near 1.47 ~ 1.55 μm was not gentle mainly because of the absorption transition of Er<sup>3+</sup> ions. In Fig. 4, the emission spectrum of the test show that: Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> could emit green 500–560 nm and red 650–700 nm, with peaks in 525, 550 and 660 nm, corresponding to <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>H<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub>, energy level transition of Er<sup>3+</sup>. Doping Co and N could broaden the absorption peak and strengthen upconversion emission.<sup>11,12</sup>

### Effects of ultrasonic intensity on the degradation of dye

In three kinds of dye (C.I. 50040, C.I. Reactive Red 1, C.I. Acid Orange 7) degradation test, the mass concentrations of the dye solutions were all 50 mg l<sup>-1</sup> and the loading qual-

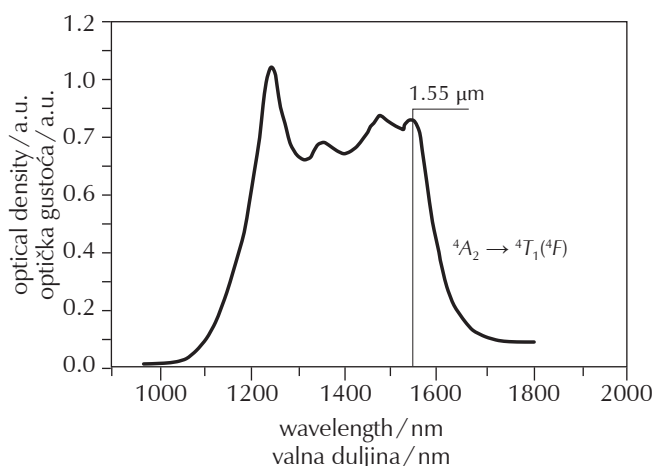


Fig. 3 – Absorption spectrum of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> crystal

Slika 3 – Apsorpcijski spektar kristala Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>

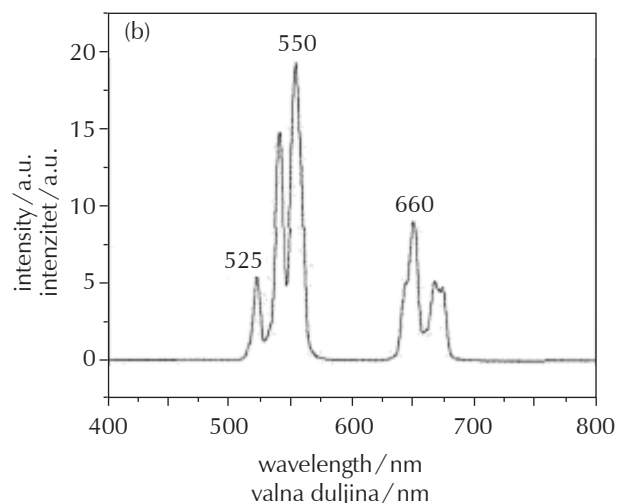


Fig. 4 – Upconversion emission spectrum of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> nanoparticles under the excitation of 980 nm diode laser

Slika 4 – Emisijski spektar uzlazne pretvorbe nanočestica Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> pri pobuđivanju diodnim laserom 980 nm

ities of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films were all 2.0 g l<sup>-1</sup>. Fig. 5 shows the degradation ratios of these three kinds of dye when ultrasonic intensities were 5, 10, 15, and 20 W cm<sup>-2</sup> respectively. At 120 minutes, the degradation ratios ( $\gamma/\gamma_0$ ) of C.I. 50040 solution reached 22.14 %, 15.36 %, 5.89 %, and 4.97 %, those of C.I. Reactive Red 1 were 24.01 %, 17.48 %, 8.24 %, and 5.84 %, and those of C.I. Acid Orange 7 were 18.79 %, 13.22 %, 5.292 %, and 4.15 %, respectively, when ultrasonic intensities were 5, 10, 15, and 20 W cm<sup>-2</sup> respectively. Apparently, the degradation ratios ( $\gamma/\gamma_0$ ) of these three kinds of dye decreased with the increasing of ultrasonic irradiation time and ultrasonic intensity. The decrease in the value of ( $\gamma/\gamma_0$ ) was more obvious when the ultrasonic intensity increased from 5 to 15 W cm<sup>-2</sup> than when the ultrasonic intensity increased from 15 to 20 W cm<sup>-2</sup>. The reason might be that,

when the ultrasonic intensity became largely excessive, the cavitation bubbles became too big in the negative phase of the sound wave to collapse sufficiently so that available ultrasonic energy decreased, thus forming a sound shield. Furthermore, when ultrasonic intensity was  $20 \text{ W cm}^{-2}$ , the ultrasonic generator could overheat and the ultrasonic probe surface could corrode significantly for cavitation. Therefore, the sound intensity,  $15 \text{ W cm}^{-2}$ , was suggested in the ultrasonic degradation experiments.

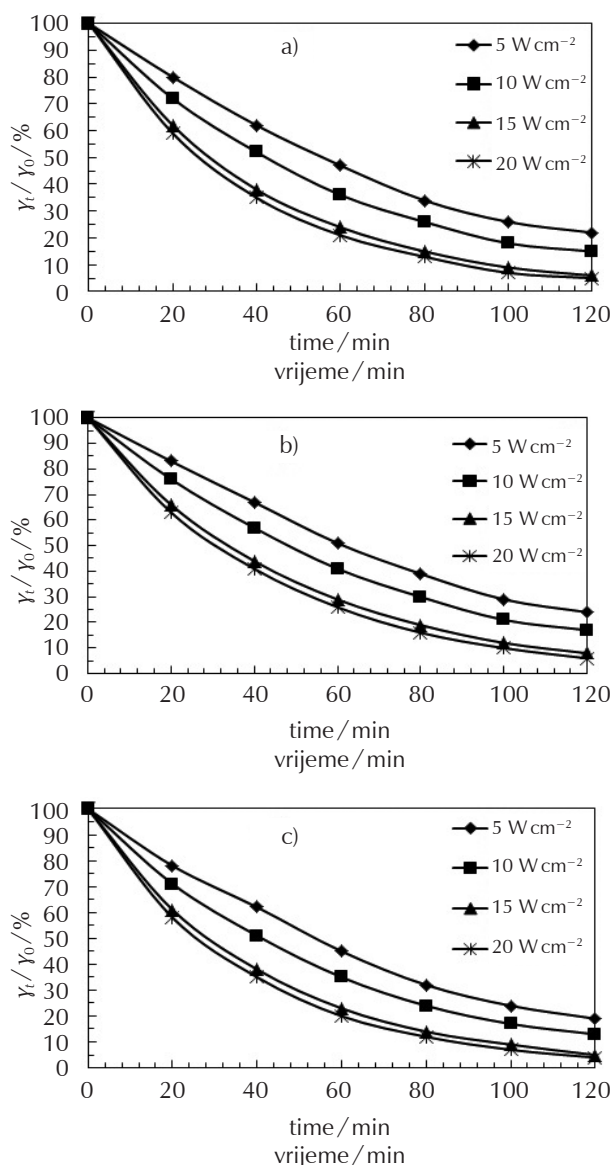


Fig. 5 – Degradation ratio of C.I. 50040 (a), C.I. Reactive Red 1 (b), and C.I. Acid Orange 7 (c) by loading  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$  films under different ultrasonic intensity irradiation (initial dye mass concentration =  $50 \text{ mg l}^{-1}$ , catalyst mass concentration =  $2.0 \text{ g l}^{-1}$ , ultrasonic intensity = 5, 10, 15,  $20 \text{ W cm}^{-2}$ )

Slika 5 – Razgradni omjer C.I. 50040 (a), C.I. Reactive Red 1 (b) i C.I. Acid Orange 7 (c) umetanjem filmova  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$  pri različitim intenzitetima ultrazvuka (početna masena koncentracija bojila =  $50 \text{ mg l}^{-1}$ , masena koncentracija katalizatora =  $2.0 \text{ g l}^{-1}$ , ultrazvučni intenzitet = 5, 10, 15,  $20 \text{ W cm}^{-2}$ )

Figs. 6a, 6b, and 6c illustrate the degradation ratios of the aqueous solutions of C.I. 50040, C.I. Reactive Red 1, and C.I. Acid Orange 7 with the time, respectively. Firstly, it can be seen that, for these three kinds of dye solutions, the

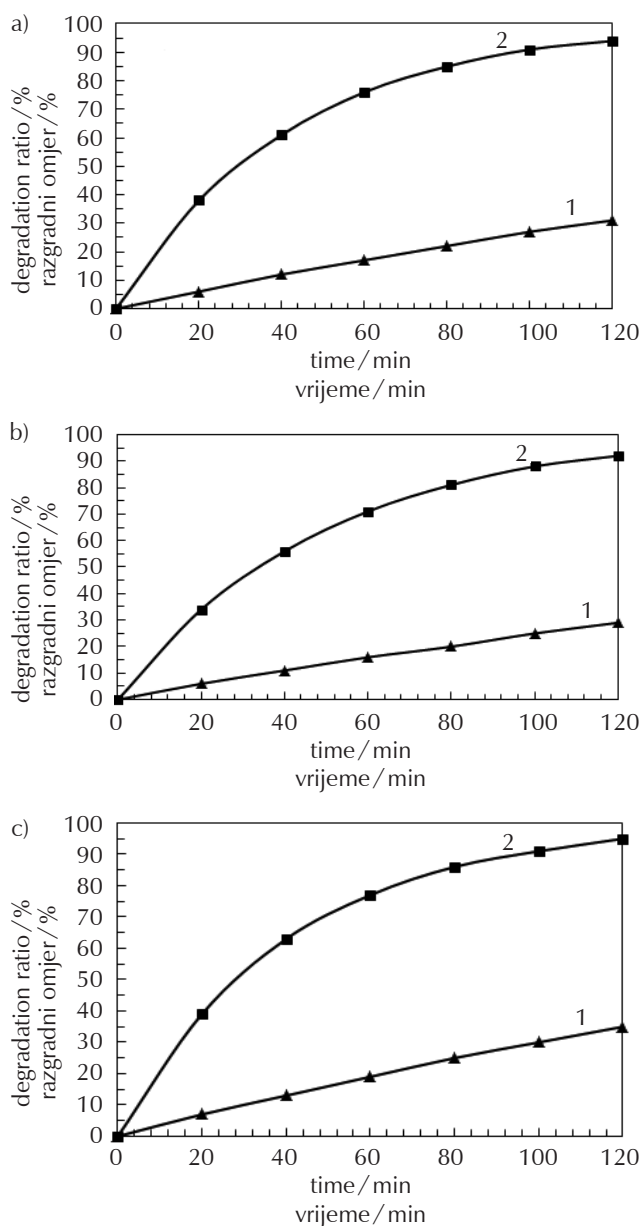


Fig. 6 – Degradation ratio of C.I.50040 (a), C.I. Reactive Red 1 (b), and C.I. Acid Orange 7 (c) solutions (in Figs. 6a, 6b, and 6c, curve 1 represents the degradation tests carried out under ultrasonic irradiation, curve 2 represents the degradation tests carried out under ultrasonic irradiation and by loading  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$  films. Initial dye mass concentration =  $50 \text{ mg l}^{-1}$ , catalyst mass concentration =  $2.0 \text{ g l}^{-1}$ , ultrasonic intensity =  $15 \text{ W cm}^{-2}$ )

Slika 6 – Razgradni omjer otopina C.I. 50040 (a), C.I. Reactive Red 1 (b) i C.I. Acid Orange 7 (c) (na slikama 6a, 6b i 6c, krivulja 1 označava da su testovi razgradnje provedeni pri ultrazvučnom zračenju, krivulja 2 označava da su testovi razgradnje provedeni pri ultrazvučnom zračenju i dodavanjem filmova  $\text{Co/N/Er}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$ . Početna masena koncentracija bojila =  $50 \text{ mg l}^{-1}$ , masena koncentracija katalizatora =  $2.0 \text{ g l}^{-1}$ , ultrazvučni intenzitet =  $15 \text{ W cm}^{-2}$ )

Table 2 – Reaction rate constants ( $k$ ) for degradation of organic dyes by ultrasonic irradiation or by ultrasonic irradiation and Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films  
 Tablica 2 – Konstante vremena reakcije ( $k$ ) za razgradnju organskih bojila ultrazvučnim zračenjem ili ultrazvučnim zračenjem i filmovima Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>

Dye Bojilo	Ultrasonic irradiation Ultrazvučno ozračenje		Ultrasonic irradiation and Co/N/ Er <sup>3+</sup> : Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> /TiO <sub>2</sub> films Ultrazvučno ozračenje i filmovi Co/N/Er <sup>3+</sup> : Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> /TiO <sub>2</sub>	
	$k/\text{min}^{-1}$	$R$	$k/\text{min}^{-1}$	$R$
C.I. 50040	0.00320	0.99961	0.0302	0.99863
C.I. Reactive Red 1	0.00296	0.99625	0.0259	0.99745
C.I. Acid Orange 7	0.00369	0.99876	0.0316	0.99878

degradation ratios all increased with the increase in time of ultrasonic irradiation. Secondly, it can be noted that the degradation ratios of C.I. 50040, C.I. Reactive Red 1, and C.I. Acid Orange 7 only under ultrasonic radiation were obviously lower than those under ultrasonic radiation and loading catalysts of Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films. This might be because ultrasonic cavitation could have produced free radicals ·OH, which could have oxidized the dye molecules, but the dye molecular structure was too stable to be degraded easily only under ultrasonic radiation. Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films had very large specific surface and thus relatively more catalytic active points. These contributed to the change of the charged properties and space configuration of dye molecules adsorbed by catalyst surface, which could improve the adsorption efficiency of surface active points, that is, make the surface radicals (·OH) oxidize the dye molecules easier. This corresponds to the bond (–N=N–) as the most active site for oxidative attack in dye molecule of C.I. 50040, C.I. Reactive Red 1, and C.I. Acid Orange 7.

Research on the sonocatalytic reaction kinetics was also conducted. The reaction rate constant and reaction order were determined by differential method.

The reaction rate equation was

$$v_t = -\frac{dc_t}{dt} = kc_t^n \quad (1)$$

where,  $v_t$  is the reaction rate at time  $t$ ,  $c_t$  is the reaction concentration at time  $t$ ,  $k$  is the reaction rate constant, and superscript  $n$  is the reaction order.

Taking logarithm on both sides of Eq. (1), we could obtain the following equation

$$\lg v_t = \lg k + n \lg c_t \quad (2)$$

According to Eq. (2), and using the reaction concentration and reaction rate measured in degradation tests, the reaction rate constant and reaction order were evaluated as shown in Table 2. The sonocatalytic degradation reactions all followed the first-order kinetics.

## Conclusions

Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films were prepared by sol-gel coating process. They were characterized by XRD, presenting the characteristic diffraction peaks of the anatase and the upconversion luminous agent, respectively. From the absorption and emission spectra figures, doping Co and N contributed to the absorption and upconversion emission effect. In the degradation tests of C.I. 50040, C.I. Reactive Red 1, and C.I. Acid Orange 7, the ultrasonic intensity 15 W cm<sup>-2</sup> was recommended. The degradation ratios of aqueous solutions of these three kinds of organic dyes by ultrasonic irradiation were obviously lower than by ultrasonic irradiation and Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films in the same conditions. The sonocatalytic degradation reactions of C.I. 50040, C.I. Reactive Red 1, and C.I. Acid Orange 7 by ultrasonic irradiation and by ultrasonic irradiation cooperating with Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films followed the first-order kinetics by differential method.

## List of abbreviations and symbols

## Popis kratica i simbola

NIR	– Near-Infrared – blisko infracrveno
UV	– Ultraviolet – ultraljubičasto
VIS	– Visible Spectroscopy – vidljiva spektroskopija
XRD	– X-Ray Diffraction – rendgenska difrakcija
$v_t$	– reaction rate at time $t$ – brzina reakcije pri vremenu $t$
$\gamma_t$	– mass concentration at time $t$ – masena koncentracija pri vremenu $t$
$k$	– reaction rate coefficient – koeficijent brzine reakcije
$n$	– reaction order – red reakcije

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## SAŽETAK

### Sinteza, karakterizacija i sonokatalitička aktivnost filmova Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> za razgradnju organskih bojila

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Proučavana je sonokatalitička razgradnja organskih bojila (C.I. 50040, C.I. Reactive Red 1, C.I. Acid Orange 7) kataliziranih filmovima Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>. Za pripremu filmova Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> korišten je sol-gel proces premazivanja. Fazni sastav, morfologija, prekursor na različitim temperaturama i svojstva emitiranja svjetlosti kalciniranog praška analizirani su rendgenskom difrakcijom (XRD), apsorpcijskim spektrom i emisijskim spektrom uzlazne pretvorbe. Rendgenska analiza praškastih uzoraka Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> obuhvatila je svjetlosni agens uzlazne pretvorbe. Analiza apsorpcijskog spektra amorfno Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> pokazala je da je dopiranjem N maksimuma vibracije istezanja vode ili hidroksilne apsorpcije, Co<sup>2+</sup> ion imao vrlo jaku apsorpciju pri valnoj duljini od 1.0 – 1.7 μm, a tranzicijska luminiscencija Er<sup>3+</sup> iona bila je samo na apsorpcijskoj vrpici Co<sup>2+</sup> iona. Emisijski spektar pokazao je da Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> može emitirati zeleno 500 – 560 nm, crveno 650 – 700 nm te maksimume od 525, 550 i 660 nm koji odgovaraju prijelazima <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> i <sup>4</sup>H<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> za Er<sup>3+</sup>. Dopirani Co i N pojačali su luminiscenciju uzlazne pretvorbe i apsorpcijski učinak. Učinak sonokatalitičke razgradnje organskih bojila s filmovima Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> bio je bolji kad je ultrazvučni intenzitet bio jednak 15 W cm<sup>-2</sup>. Razgradni omjeri vodenih otopina ovih triju vrsta organskih bojila ultrazvučnim ozračenjem bili su znatno niži od ultrazvučnog ozračenja zajedno s filmovima Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> pri istim uvjetima. Kinetika razgradnje organskih bojila ultrazvučnim ozračenjem i ultrazvučnim ozračenjem s filmovima Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> pratila je reakciju prvog reda.

#### Ključne riječi

Co/N/Er<sup>3+</sup> : Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>, emisijski spektar uzlazne pretvorbe, sonokataliza, razgradnja bojila

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