

*Received July 18, 2011, reviewed, accepted September 1, 2011*

## **CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF RARE EARTH METAL-DOPED TITANIUM DIOXIDE**

Joanna RESZCZYNSKA \*, Anna IWULSKA \*\*, Gerard SLIWINSKI \*\*,  
Adriana ZALESKA \*

\* Department of Chemical Technology, Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland, e-mail: adriana.zaleska@pg.gda.pl

\*\* Photophysics Department, Institute of Fluid-flow Machinery, Polish Academy of Sciences, Gdansk, Poland

**Abstract.** The aim of this research was to prepare rare metal (Er, Yb)-modified TiO<sub>2</sub> nanoparticles by a sol-gel method. The obtained nanoparticles were characterized by BET measurements, UV-Vis spectra and the Laser-induced fluorescence (LIF) method. Visible light photocatalytic activity of the sample was studied by photodegradation of phenol while considering the influence of the dopant concentration. The obtained results showed that a smaller amount of the dopant gave better photocatalytic activity of a semiconductor. The absorption spectra of Yb<sup>3+</sup>-doped and Er<sup>3+</sup>-TiO<sub>2</sub> samples show stronger absorption in the UV-Vis region than pure TiO<sub>2</sub>. The presence of erbium was found more beneficial for visible light activation of TiO<sub>2</sub> doped photocatalysts than ytterbium.

*keywords: photocatalysis, rare earth metal, modified TiO<sub>2</sub>, luminescence*

### **1. Introduction**

Heterogeneous photocatalytic oxidation, developed in the 1970s, has attracted considerable attention particularly when used under solar light (Teh and Mohamed, 2011). Over the past 10 years, the semiconductor TiO<sub>2</sub>, as a photocatalyst, has become the focus of numerous studies owing to its attractive characteristics and applications in the treatment of environmental contaminants (Lin and Yu, 1998). There are a lot of applications of TiO<sub>2</sub> for photodegradation of organic compounds (Hoffmann et al., 1995), inorganic reagents (Bakarat et al., 2004), removing odors from closed spaces, and self-cleaning surfaces (Fujishima et al., 2000). There are some examples of photocatalytic decomposition of water (Khan et al., 2002) and photoconversion of CO<sub>2</sub> (Tan et al., 2006) for methane in the presence of TiO<sub>2</sub>.

In this respect the most important challenge is to increase the efficiency of the processes of photoconversion and extension of the spectral sensitivity of TiO<sub>2</sub>. In this context, most of the work carried out in the world in recent years has aimed at

modification of  $\text{TiO}_2$ , in order to obtain the activated photocatalyst with visible light. The  $\text{TiO}_2$ -based photocatalysts, exhibiting higher activity under UV or visible light, can be obtained by: addition of transition metal ions, preparation of reduced forms of  $\text{TiO}_{2-x}$  (Takeuchi et al., 2000), sensitization of  $\text{TiO}_2$  using dyes (Chatterjee and Mahata, 2001),  $\text{TiO}_2$  sensitization using a smaller width of the semiconductor band gap  $E_g$  (Hirai et al., 2001), and doping non-metals (Asahi et al., 2001; Ohno et al., 2003; Janus and Morawski, 2007; Korosi and Dekany, 2006; Zaleska et al., 2007).

Rare earth elements are especially suitable for optical applications, since they have unfilled 4f and 5d shells. The effect of upconversion or Anti-Stokes emission is generally known from laser physics. The light of lower energy is up-converted in the light with a shorter wavelength. Several mechanisms are possible, which act either alone or in combination. The three main excitation processes are: excited-state absorption, energy-transfer upconversion and photon avalanche (Feng et al., 2008). Cacciotti et al. (2011) fabricated Tb-dopant and Yb-dopant  $\text{TiO}_2$  by electrospinning technique. All the samples showed luminescent properties. Yang et al. (2011) prepared inverse opal photonic crystals of  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  co-doped  $\text{TiO}_2$  ( $\text{TiO}_2\text{:Yb, Er}$ ) by a self-assembly technique in combination with a sol-gel method. They observed luminescence properties of the inverse opals. Gao et al. (2011) synthesized  $\text{Er}^{3+}\text{:YAlO}_3/\text{Fe}$ -doped  $\text{TiO}_2\text{-ZnO}$  composite by ultrasonic dispersion and a liquid boiling method. They showed that  $\text{Er}^{3+}\text{:YAlO}_3$  can transform the visible light in solar energy into ultraviolet light, satisfying the requirement of  $\text{TiO}_2\text{-ZnO}$  composite for photocatalytic degradation (Acid Red B dye). Wang et al. (2006, 2007a; 2007b) and Feng et al. (2008) mixed upconversion materials with  $\text{TiO}_2$  and reported that the photocatalytic activity of the upconversion-doped  $\text{TiO}_2$  is higher than that of the undoped one. Upconversion materials, which were synthesized without Y-Al-O compounds, were only reported by Shang et al. (2008). They prepared  $\text{Er}^{3+}\text{-Yb}^{3+}$  co-doped  $\text{TiO}_2$  nanocrystals by a sol-gel method. However, the activity of the obtained photocatalysts were examined only in the process of the degradation of dyes (which may act as sensitizer and thereby cause a misstatement of the effectiveness assessment of the degradation). In accessible literature there is no available information on the stability of photocatalysts (the possibility of recycling and stability of photocatalysts during storage).

Here we report a preparation method and characteristics of erbium- and ytterbium-modified  $\text{TiO}_2$  photocatalysts. Rare earth metal-doped  $\text{TiO}_2$  was prepared by a sol-gel method.

## 2. Experimental

### 2.1. Materials and instruments

Titanium isopropoxide (pure p.a.) was purchased from Aldrich and used as titanium source for the preparation of  $\text{TiO}_2$  nanoparticles.  $\text{Er}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  and  $\text{Yb}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  salts were freshly prepared by the reaction of  $\text{Er}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  with



nitric acid.  $\text{Er}_2\text{O}_3$  (99.9%) and  $\text{Yb}_2\text{O}_3$  (99.9%) were obtained from Sigma Aldrich while  $\text{TiO}_2$  P25 from Evonik, Germany (surface area  $50 \text{ m}^2/\text{g}$ ). All the chemicals were used as received without further purification. Deionized water was used for all the reactions and treatment processes.

Nitrogen adsorption-desorption isotherms were recorded at liquid nitrogen temperature (77 K) on a Micromeritics Gemini V (model 2365) and specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method.

The diffuse reflectance spectra DRS were characterized using UV–Vis spectrometer (Labomed, Inc.) equipped with an integrating sphere accessory for diffuse reflectance.

To measure the fluorescence spectra (LIF, Laser-induced fluorescence) a UV-Vis spectrometer equipped with a SR-303i monochromator and ICCD camera iStar DH 740 using a diffraction grating 600 lines/mm were used. The quantity counts were: 100 Laser: Nd: YAG laser with a wavelength of 532 nm.

## 2.2. Preparation of doped $\text{TiO}_2$ photocatalysts

$\text{TiO}_2$ -based photocatalysts were obtained according to the procedures presented by a simplified block diagram in Fig. 1. A sample of  $12.2 \text{ cm}^3$  titanium isopropoxide was added to the mixture of  $6.0 \text{ cm}^3$  acetic acid and  $48 \text{ cm}^3$  ethanol. The sol was stirred for 10 min, then  $3.0 \text{ cm}^3$  water was added dropwise. Then, a certain amount of  $\text{Er}(\text{NO}_3)_3$  and  $\text{Yb}(\text{NO}_3)_3$  was added and the sol was stirred for one more hour. The obtained gel was dried at  $60^\circ\text{C}$  for 20 h in a vacuum oven and ground to obtain powder. The heat-treatment of  $400^\circ\text{C}$  for 2.5 h in the air was applied to the sample. The concentration of metal precursors, which varied from 0.25 to 1.0 mol.% was related to the concentration of TIP in the sol-gel system.

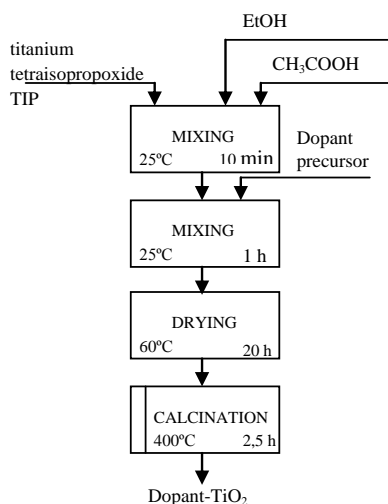


Fig. 1. Block diagram of RE-doped  $\text{TiO}_2$  prepared by a sol-gel method

### 2.3. Measurements of photocatalytic activity

The photocatalytic activity of RE-TiO<sub>2</sub> powders in visible light was estimated by measuring the decomposition rate of phenol (0.21 mmol/dm<sup>3</sup>) in an aqueous solution. Photocatalytic degradation runs were preceded by blind tests in the absence of a catalyst or illumination. Twenty five milliliters of catalyst suspension (125 mg) were stirred using a magnetic stirrer and aerated (5 dm<sup>3</sup>/h) prior and during the photocatalytic process. Aliquots of 1.0 cm<sup>3</sup> of the aqueous suspension were collected at regular time periods during irradiation and filtered through syringe filters (Ø = 0.2 mm) to remove catalyst particles. Phenol concentration was estimated by a colorimetric method using UV-Vis spectrophotometer (DU-520, Beckman). The suspension was irradiated using 1000 W Xenon lamp (Oriel), which emits both UV and Vis light. To limit the irradiation wavelength, the light beam was passed through GG400 filter to cut-off wavelengths shorter than 400 nm.

### 3. Results and discussion

Table 1 presents the BET surface area, pore volume and photocatalytic activity results for the erbium- and ytterbium-doped TiO<sub>2</sub> nanoparticles. The Er<sup>3+</sup>-TiO<sub>2</sub> photocatalyst modified with 0.5 mol.% of Er has the lowest BET surface area and pore volume of about 113 m<sup>2</sup>/g and 0.056 cm<sup>3</sup>/g, respectively. The Yb<sup>3+</sup>-TiO<sub>2</sub>, modified with 0.5 mol.% Yb, has the highest surface area and pore volume equal to about 132 m<sup>2</sup>/g and 0.065 cm<sup>3</sup>/g, respectively. For other Er<sup>3+</sup>-TiO<sub>2</sub> and Yb<sup>3+</sup>-TiO<sub>2</sub> samples containing from 0.25 to 1.0 mol.% of metal the surface areas varied from 119 to 126m<sup>2</sup>/g. It was observed that metal dopant affects the surface area of TiO<sub>2</sub> powder samples. The obtained results indicated that other parameters, such as erbium or ytterbium presence cause their enhancement in photoactivity, rather than the surface area.

Table 1. BET surface area, pore volume and photocatalytic activity of RE-TiO<sub>2</sub> photocatalysts

Photocatalysts type	Amount of metal precursor [mol %]	S <sub>BET</sub> [m <sup>2</sup> /g]	Pore volume [cm <sup>3</sup> /g]	Phenol degradation after 1h exposure to Vis irradiation (λ>400 nm) [%]
TiO <sub>2</sub>	-	118	0.058	24
Er <sup>3+</sup> -TiO <sub>2</sub>	0.25	126	0.062	38
Er <sup>3+</sup> -TiO <sub>2</sub>	0.5	113	0.056	31
Er <sup>3+</sup> -TiO <sub>2</sub>	1.0	123	0.061	21
Yb <sup>3+</sup> -TiO <sub>2</sub>	0.25	119	0.059	25
Yb <sup>3+</sup> -TiO <sub>2</sub>	0.5	132	0.065	31
Yb <sup>3+</sup> -TiO <sub>2</sub>	1.0	125	0.061	26

To study the optical absorption properties of as-prepared samples, UV-Vis absorption spectra in the range 350 – 700 nm were investigated, and the results are shown in Fig. 2. It can be seen that the modification of titania with erbium significantly affected the light absorption property of the photocatalysts. Furthermore,



it can be seen that there are three typical absorption peaks located at 490, 535 and 655 nm. The spectrum in Fig. 2 is characteristic for  $\text{Er}^{3+}$ -doped colloid with absorption bands identified with the transitions from the  $^4\text{I}_{15/2}$  ground state to the excited states of the  $\text{Er}^{3+}$  ions (Pang et al., 2010).

The absorption spectra of  $\text{Yb}^{3+}$ -doped and  $\text{Er}^{3+}$ - $\text{TiO}_2$  samples show stronger absorption in the UV-Vis region than commercially available P25.

The photoluminescence spectra were measured on  $\text{Er}^{3+}$ - $\text{TiO}_2$  and  $\text{Yb}^{3+}$ - $\text{TiO}_2$  samples under excitation at 532 nm. Emission bands were observed at 670 nm for erbium and at 580 and 640 nm for ytterbium. Figure 3 shows the photoluminescence spectra of the prepared powders. These spectra show the concentration quenching of erbium and ytterbium luminescence, as expected. When the concentration of rare earth metal decreased, then erbium and ytterbium emission was enhanced.

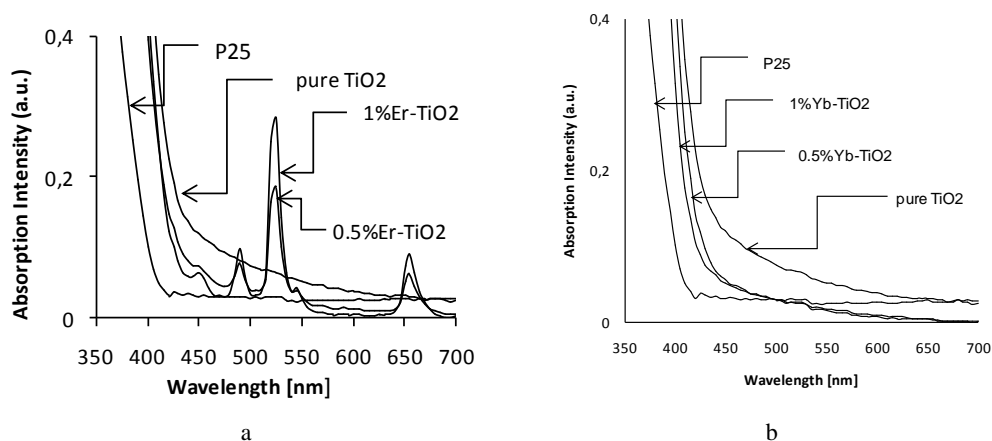


Fig. 2. Absorption properties of RE- $\text{TiO}_2$  prepared by a sol-gel method, a)  $\text{Er}^{3+}$ - $\text{TiO}_2$ , b)  $\text{Yb}^{3+}$ - $\text{TiO}_2$

The photocatalytic activity of the rare earth metal-doped  $\text{TiO}_2$  nanoparticles was evaluated by measuring the decomposition of phenol. The efficiency of phenol degradation after 60 min of exposure to Vis irradiation in the presence of  $\text{Er}^{3+}$ - $\text{TiO}_2$  and  $\text{Yb}^{3+}$ - $\text{TiO}_2$  nanoparticles is presented in Table 1 and Fig. 4.

The photodegradation efficiency under visible light decreased with the increase in the ytterbium loading up to 0.5 mol.% and then decreased. When erbium was the dopant, the photodegradation efficiency under visible light decreased with the increase in the erbium loading up to 0.25 mol.%. The efficiency of phenol decomposition measured in the presence of the sample 0.25% $\text{Er}^{3+}$ - $\text{TiO}_2$  after 60 min of irradiation was 38%. It indicates that the presence of erbium was more beneficial for visible light activation of  $\text{TiO}_2$  doped photocatalysts than ytterbium, where maximum efficiency of phenol decomposition was 31% for the sample 0.5% $\text{Yb}^{3+}$ - $\text{TiO}_2$ . All rare earth metal-doped photocatalysts have better photocatalytic activity than the undoped ones.

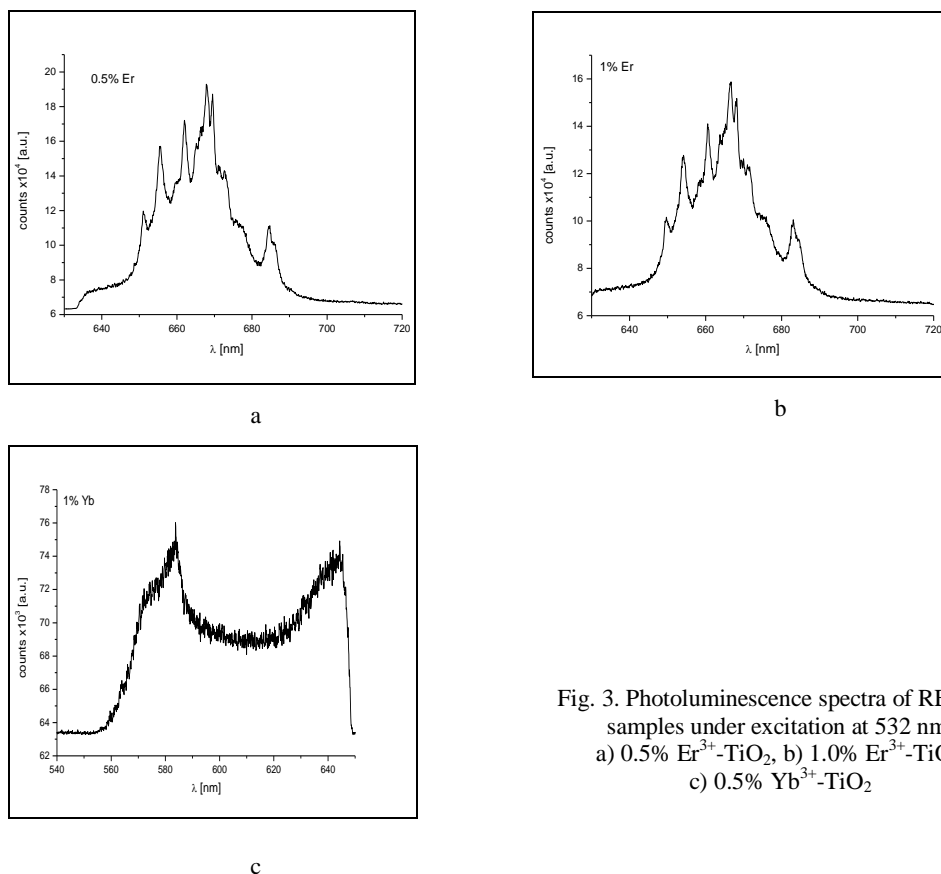


Fig. 3. Photoluminescence spectra of RE-TiO<sub>2</sub> samples under excitation at 532 nm, a) 0.5% Er<sup>3+</sup>-TiO<sub>2</sub>, b) 1.0% Er<sup>3+</sup>-TiO<sub>2</sub>, c) 0.5% Yb<sup>3+</sup>-TiO<sub>2</sub>

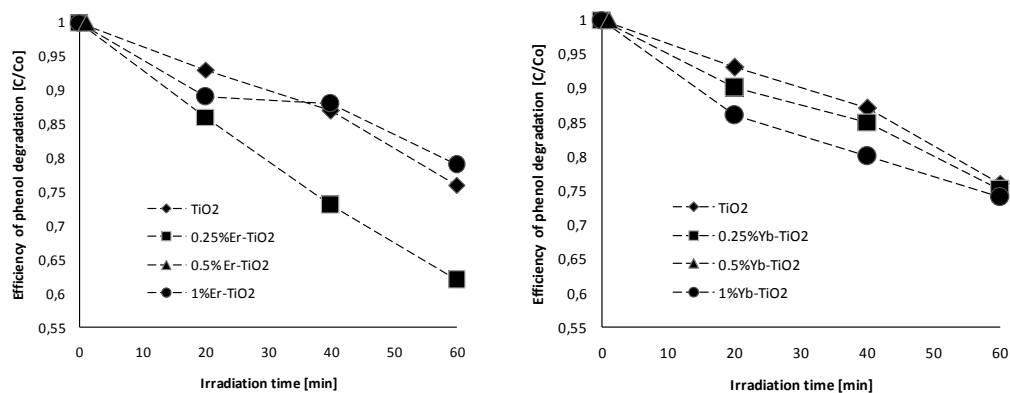


Fig. 4. Efficiency of phenol photodegradation in the presence of RE-doped TiO<sub>2</sub> under visible light ( $\lambda > 400$  nm). Experimental conditions:  $C_0 = 0.21$  mM,  $m(\text{TiO}_2) = 125$  mg,  $T = 10^\circ\text{C}$ ,  $Q_{\text{air}} = 5$  dm<sup>3</sup>/h, a) Er<sup>3+</sup>-TiO<sub>2</sub>, b) Yb<sup>3+</sup>-TiO<sub>2</sub>

### 3. Conclusion

The photocatalysts based on TiO<sub>2</sub> and doped with rare earth metal have luminescence properties. The effect of metal modification on photocatalytic activity depends on the type of metal and metal precursor concentration used during the preparation. It was found that titania surface modification with erbium and ytterbium caused an increase of the photocatalytic activity under visible irradiation and it was observed that a metal dopant affects the surface area of TiO<sub>2</sub> powder samples. The absorption spectra of Yb<sup>3+</sup>-doped and Er<sup>3+</sup>-TiO<sub>2</sub> samples show stronger absorption in the UV–Vis region than commercially available TiO<sub>2</sub> P25. It can be seen that for Er<sup>3+</sup>-TiO<sub>2</sub> there are three typical absorption peaks located at 490, 535 and 655 nm.

### Acknowledgments

This work was supported by Polish Ministry of Science and Higher Education (No. N N523 420137).

### References

- ASAHI R., MORIKAWA T., OHWAKI T., AOKI K., TAGA Y., 2001, Visible-light photocatalysis in nitrogen-doped titanium oxides, *Science* 293, 269–271.
- BAKARAT M.A., CHEN Y.T., HUANG C.P., 2004, Removal of Toxic Cyanide and Cu(II) Ions from Water by Illuminated TiO<sub>2</sub> Catalyst, *Appl. Catal. B* 53, 13–20.
- CACCIOTTI I., BIANCO A., PEZZOTTI G., GUSMANO G., 2011, Terbium and ytterbium-doped titania luminescent nanofibers by means of electrospinning technique, *Mat. Chem. Phys.* 126, 532–541.
- CHATTERJEE D., MAHATA A., 2001, Demineralization of organic pollutants on the dye modified TiO<sub>2</sub> semiconductor particulate system using visible light, *Appl. Catal. B Environ.* 33, 119–125.
- FENG G., LIU S., XIU Z., ZHANG Y., YU J., CHEN Y., WANG P., YU X., 2008, Visible light photocatalytic activities of TiO<sub>2</sub> nanocrystals doped with up-conversion luminescence agent, *J. Phys. Chem. C* 112, 13692–13699.
- FUJISHIMA A., RAO T.N., TRYK D.A., 2000, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C: Photochem. Rev.* 1, 1–21.
- GAO J., LUAN X., WANG J., WANG B., LI K., LI Y., KANG P., HAN G., 2011, Preparation of Er<sup>3+</sup>:YAIO<sub>3</sub>/Fe-doped TiO<sub>2</sub>-ZnO and its application in photocatalytic degradation of dyes under solar light irradiation, *Chem. Eng. J.* 268, 68–75.
- HIRAI T., SUZUKI K., KOMASAWA I., 2001, Preparation and photocatalytic properties of composite CdS nanoparticles-titanium dioxide particles, *J. Colloid Interface Sci.* 244, 262–265.
- HOFFMANN M.R., MARTIN S.T., CHOI W., BAHNEMANN D.W., 1995, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95, 69–96.
- JANUS M., MORAWSKI A.W., 2007, New method of improving photocatalytic activity of commercial Degussa P25 for azo dyes decomposition, *Appl. Catal. B* 75, 118–123.
- KHAN S.U., AL-SHAHRY M., INGLER W.B. JR., 2002, Efficient photochemical water splitting by a chemically modified n-TiO<sub>2</sub>, *Science* 297, 2243–2245.
- KOROSI L., DEKANY I., 2006, Preparation and investigation of structural and photocatalytic properties of phosphate modified titanium dioxide, *Colloids Surf., A* 280, 146–154.
- LIN J., YU J.C., 1998, An investigation on photocatalytic activities of mixed TiO<sub>2</sub>-rare earth oxides for the oxidation of acetone in air, *J. Photochem. Photobiol. A: Chem.* 116, 63–67.
- NAKAMURA I., NEGISHI N., KUTSUNA S., IHARA T., SUGIHARA S., TAKEUCHI K., 2000, Role of oxygen vacancy in the plasma-treated TiO<sub>2</sub> photocatalyst with visible light activity for NO removal, *J. Mol. Catal. A: Chem.* 161, 205–212.



- OHNO T, MITSUI T., MATSUMURA M., 2003, Photocatalytic activity of S-doped TiO<sub>2</sub> photocatalyst under visible light, *Chem. Lett.* 32, 364–365.
- PANG S., LI X., SHI Z., YANG G., CUI Z., 2010, Preparation and characterization of sol-gel derived Er<sup>3+</sup>-Yb<sup>3+</sup> codoped SiO<sub>2</sub>/TiO<sub>2</sub> core-shell nanoparticles, *Mat. Lett.* 64, 846–848.
- SHANG Q., YU H., KONG X., WANG H., WANG X., SUN Y., ZHANG Y., ZENG Q., 2008, Green and red up-conversion emissions of Er<sup>3+</sup>-Yb<sup>3+</sup> Co-doped TiO<sub>2</sub> nanocrystals prepared by sol-gel method. *J. Lumin.* 128, 1211–1216.
- TAN S.S., ZOU L., HU E., 2006, Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO<sub>2</sub> pellets, *Cataly. Tod.* 115, 269–273.
- TEH C.M., MOHAMED A.R., 2011, Roles of titanium dioxide and ion-doped titanium dioxide on photocatalytic degradation of organic pollutants (phenolic compounds and dyes) in aqueous solutions: A review, *J. All. Comp.* 509, 1648-1660.
- WANG J., LI R., ZHANG Z., SUN W., XU R., XIE Y., XING Z., ZHANG X., 2007a, Efficient photocatalytic degradation of organic dyes over titanium dioxide coating upconversion luminescence agent under visible and sunlight irradiation, *Appl. Cat. A, Gen.* 334, 227–233.
- WANG J., MA T., ZHANG G., ZHANG Z., ZHANG X., JIANG Y., ZHAO G., ZHANG P., 2007b, Preparation of novel nanometer TiO<sub>2</sub> catalyst doped with upconversion luminescence agent and investigation on degradation of acid red B dye using visible light, *Cat. Comm.* 8, 607–611.
- WANG J., WEN F.Y., ZHANG Z.H., ZHANG X.D., PAN Z.J., ZHANG P., KANG P.L., TONG J., WANG L., XU L., 2006, Investigation on degradation of dyestuff wastewater using visible light in the presence of a novel nano TiO<sub>2</sub> catalyst doped with upconversion luminescence agent, *J. Photochem. Photobiol., A: Chem.* 180, 189–195.
- YANG Z., ZHU K., SONG Z., ZHOU D., YIN Z., QIU J., 2011, Preparation and upconversion emission properties of TiO<sub>2</sub>:Yb, Er inverse opals, *Sol. Stat. Comm.* 151, 364–367.
- ZALESKA A., SOBCZAK J.W., GRABOWSKA E., HUPKA J., 2007, Preparation and photocatalytic activity of boron-modified TiO<sub>2</sub> under UV and visible light, *Appl. Catal. B* 78, 92–100.

