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

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Abstract. The aim of this research was to prepare rare metal (Er, Yb)-modified TiO_2 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^{3+}-doped and Er^{3+}-TiO_2 samples show stronger absorption in the UV–Vis region than pure TiO_2. The presence of erbium was found more beneficial for visible light activation of TiO_2 doped photocatalysts than ytterbium.

keywords: photocatalysis, rare earth metal, modified TiO_2, 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_2, 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_2 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_2 (Tan et al., 2006) for methane in the presence of TiO_2.

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_2. In this context, most of the work carried out in the world in recent years has aimed at modification of TiO_2, in order to obtain the activated photocatalyst with visible light. The 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 TiO_{2-x} (Takeuchi et al., 2000), sensitization of TiO_2 using dyes (Chatterjee and Mahata, 2001), 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 TiO_2 by electrospinning technique. All the samples showed luminescent properties. Yang et al. (2011) prepared inverse opal photonic crystals of Yb^{3+}, Er^{3+} co-doped TiO_2 (TiO_2: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 $Er^{3+}:YAlO_3$/Fe-doped TiO_2-ZnO composite by ultrasonic dispersion and a liquid boiling method. They showed that $Er^{3+}:YAlO_3$ can transform the visible light in solar energy into ultraviolet light, satisfying the requirement of TiO_2-ZnO compose for photocatalytic degradation (Acid Red B dye). Wang et al. (2006, 2007a; 2007b) and Feng et al. (2008) mixed upconversion materials with TiO_2 and reported that the photocatalytic activity of the upconversion-doped 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 Er^{3+}-Yb^{3+} co-doped 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 TiO_2 photocatalysts. Rare earth metal-doped 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 TiO_2 nanoparticles. $Er(NO_3)_3 \cdot 6H_2O$ and $Yb(NO_3)_3 \cdot 6H_2O$ salts were freshly prepared by the reaction of Er_2O_3 and Yb_2O_3 with nitric acid. Er_2O_3 (99.9%) and Yb_2O_3 (99.9%) were obtained from Sigma Aldrich while TiO_2 P25 from Evonik, Germany (surface area 50 m^2/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 TiO_2 photocatalysts

TiO_2-based photocatalysts were obtained according to the procedures presented by a simplified block diagram in Fig. 1. A sample of 12.2 cm^3 titanium isopropoxide was added to the mixture of 6.0 cm^3 acetic acid and 48 cm^3 ethanol. The sol was stirred for 10 min, then 3.0 cm^3 water was added dropwise. Then, a certain amount of $Er(NO_3)_3$ and $Yb(NO_3)_3$ was added and the sol was stirred for one more hour. The obtained gel was dried at 60ºC for 20 h in a vacuum oven and ground to obtain powder. The heat-treatment of 400ºC 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.

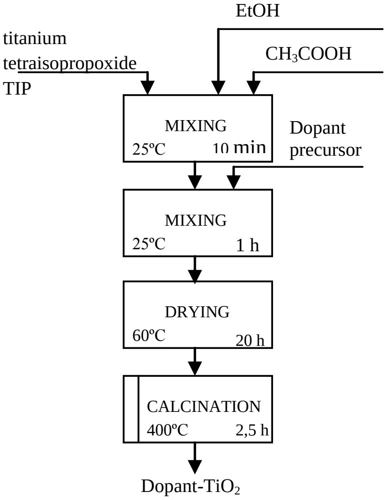


Fig. 1. Block diagram of RE-doped TiO_2 prepared by a sol-gel method

2.3. Measurements of photocatalytic activity

The photocatalytic activity of RE-TiO_2 powders in visible light was estimated by measuring the decomposition rate of phenol (0.21 mmol/dm^3) 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^3/h) prior and during the photocatalytic process. Aliquots of 1.0 cm^3 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_2 nanoparticles. The Er^{3+}-TiO_2 photocatalyst modified with 0.5 mol.% of Er has the lowest BET surface area and pore volume of about 113 m^2/g and 0.056 cm^3/g, respectively. The Yb^{3+} -TiO_2, modified with 0.5 mol.% Yb, has the highest surface area and pore volume equal to about 132 m^2/g and 0.065 cm^3/g, respectively. For other Er^{3+}-TiO_2 and Yb^{3+}-TiO_2 samples containing from 0.25 to 1.0 mol.% of metal the surface areas varied from 119 to 126m^2/g. It was observed that metal dopant affects the surface area of TiO_2 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.

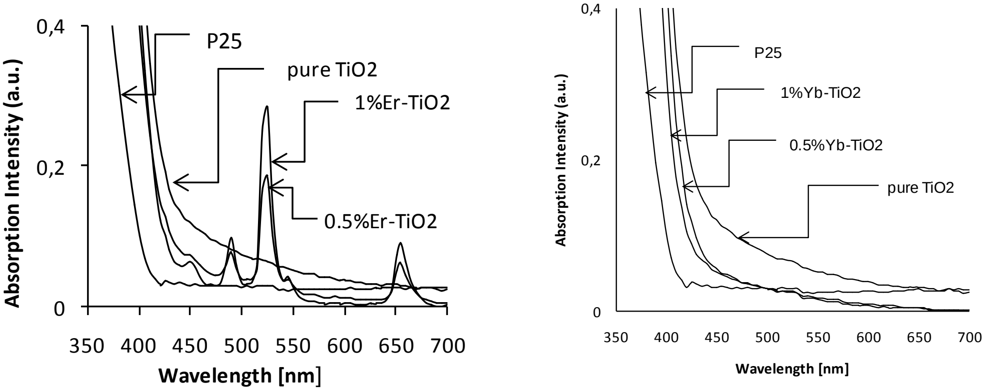
Table 1. BET surface area, pore volume and photocatalytic activity of RE-TiO_2 photocatalysts

Photocatalysts type	Amount of metal precursor [mol %]	S_{BET} [m^2/g]	Pore volume [cm^3/g]	Phenol degradation after 1h exposure to Vis irradiation (λ>400 nm) [%]
TiO_2	-	118	0.058	24
Er^{3+}–TiO_2	0.25	126	0.062	38
Er^{3+}–TiO_2	0.5	113	0.056	31
Er^{3+}–TiO_2	1.0	123	0.061	21
Yb^{3+}–TiO_2	0.25	119	0.059	25
Yb^{3+}–TiO_2	0.5	132	0.065	31
Yb^{3+}–TiO_2	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 Er^{3+}-doped colloid with absorption bands identified with the transitions from the $^4I_{15/2}$ ground state to the excited states of the Er^{3+} ions (Pang et al., 2010).

The absorption spectra of Yb^{3+}-doped and Er^{3+}-TiO_2 samples show stronger absorption in the UV–Vis region than commercially available P25.

The photoluminescence spectra were measured on Er^{3+}-TiO_2 and Yb^{3+}-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.

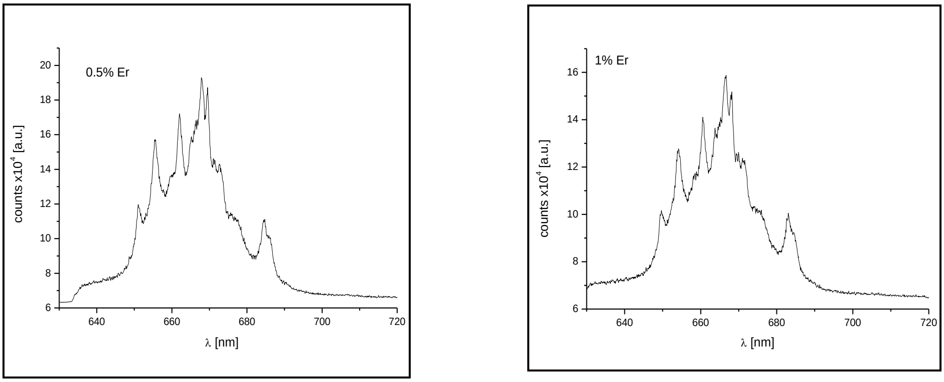


a b

Fig. 2. Absorption properties of RE-TiO_2 prepared by a sol-gel method, a) Er^{3+}- TiO_2, b) Yb^{3+}-TiO_2

The photocatalytic activity of the rare earth metal-doped 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 Er^{3+}-TiO_2 and Yb^{3+}-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%Er^{3+}-TiO_2 after 60 min of irradiation was 38%. It indicates that the presence of erbium was more beneficial for visible light activation of TiO_2 doped photocatalysts than ytterbium, where maximum efficiency of phenol decomposition was 31% for the sample 0.5%Yb^{3+}-TiO_2. All rare earth metal-doped photocatalysts have better photocatalytic activity than the undoped ones.



a

b

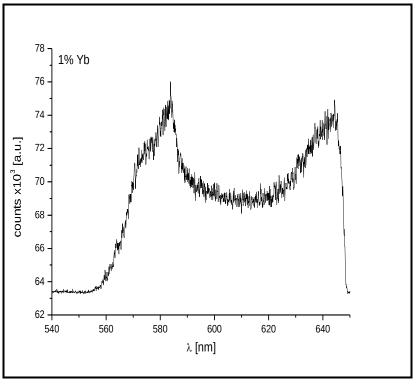


Fig. 3. Photoluminescence spectra of RE-TiO_2 samples under excitation at 532 nm, a) 0.5% Er^{3+}-TiO_2, b) 1.0% Er^{3+}-TiO_2, c) 0.5% Yb^{3+}-TiO_2

c

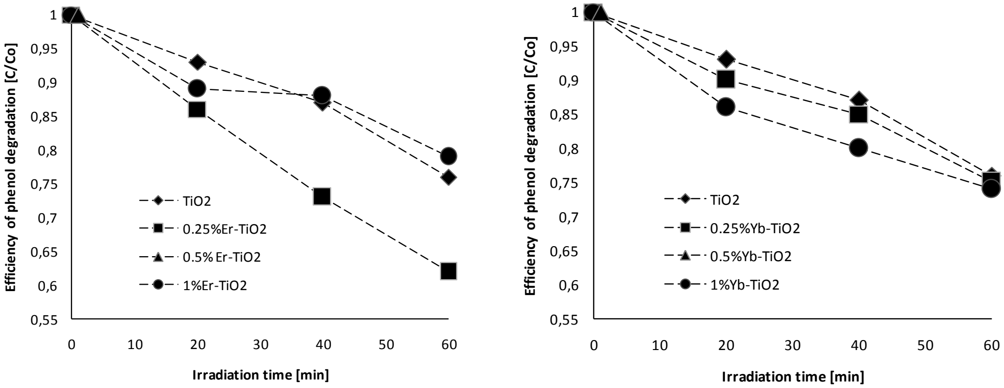


Fig. 4. Efficiency of phenol photodegradation in the presence of RE-doped TiO_2 under visible light (λ>400 nm). Experimental conditions: C_o=0.21 mM, m (TiO_2)=125 mg, T=10˚C, Q_{air}=5 dm^3/h, a) Er^{3+}-TiO_2, b) Yb^{3+}-TiO_2

3. Conclusion

The photocatalysts based on TiO_2 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_2 powder samples. The absorption spectra of Yb^{3+}-doped and Er^{3+}-TiO_2 samples show stronger absorption in the UV–Vis region than commercially available TiO_2 P25. It can be seen that for Er^{3+}-TiO_2 there are three typical absorption peaks located at 490, 535 and 655 nm.

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