Journal of Engineering and Fundamentals
Vol. 2(1), pp. 26-37, June , 2015
Available online at <http://www.tjef.net>
ISSN: 2149-0325
<http://dx.doi.org/10.17530/jef.15.07.2.1>

Photocatalytic Hydrogen Production with Erbium Doped Titania Powders

Hüsnü Arda Yurtsever*

Chemical Engineering Department, Izmir Institute of Technology, Izmir, Turkey

Muhsin Çiftçioğlu

Chemical Engineering Department, Izmir Institute of Technology, Izmir, Turkey

Article history

Received:
15.03.2015

Received in revised form:
18.05.2015

Accepted:
26.05.2015

Key words:

titania; erbium; photocatalytic activity; hydrogen production; sol-gel.

Erbium (Er) doped titania (TiO_2) powders were prepared by sol-gel technique. The effect of Er doping level on the nanophase structure, optical properties and photocatalytic hydrogen production activity was investigated throughout this study. X-ray diffraction (XRD), UV-VIS diffuse reflectance spectroscopy (UV-VIS DRS), photoluminescence (PL) and N_2 adsorption-desorption analyses were conducted for the determination of the nanostructure and optical properties of the prepared powders. It was found that Er doping inhibited the phase transformation of anatase to rutile, enhanced the visible light absorption and increased the surface area of TiO_2 . Photocatalytic activity experiments indicated that the highest hydrogen yield was obtained with 0.5% Er doped TiO_2 which was 40 and 1.5 times higher than undoped TiO_2 on the basis of weight and surface area of the photocatalyst, respectively. The increased photocatalytic activity was attributed to a possible optimization of the nanophase structure which increased anatase weight fraction, enhanced light absorption and decreased the recombination rate of electron-hole pairs by forming oxygen deficiencies in the nanostructure.

* Correspondence: Fax: +90 232 750 6015, Tel: +90 232 750 6648, E-mail: husnuarda@gmail.com

1. Introduction

In recent years global warming has become the most outstanding environmental problem. Intensive research on reducing carbon emissions have been carried out and are still popular among researchers [1]. Artificial photosynthesis systems are designed to reduce CO₂ in the atmosphere which store the sunlight energy in the form of chemical energy. Fujishima and Honda conducted the pioneering studies in 1970s to produce hydrogen by water splitting via photocatalytic processes by using titania (TiO₂) and solar energy [2]. TiO₂ based materials are mostly preferred materials for artificial photosynthesis applications towards solving environmental and energy problems by utilizing solar energy due to its chemical, optical and photocatalytic properties. However wide bandgap of TiO₂ (anatase 3.2 eV, rutile 3.0 eV) is a drawback limiting the light absorption to only UV region representing 10% of the solar radiation [3]. There are several methods for the enhancement of light absorption of TiO₂ such as doping, combining with low bandgap materials, dye sensitization or surface modification. Doped TiO₂ phases were synthesized with various methods in many studies for the use in photocatalytic water splitting in the last 15 years. A comprehensive review was conducted by Ni et al. [4] including the mechanism of photocatalytic water splitting and TiO₂ modification methods to improve the hydrogen production activity. Recent studies have shown that the photocatalytic hydrogen production activity of TiO₂ can be enhanced by modifying the initial particle size and anatase-rutile ratio of TiO₂ [5], Cu₂O sensitization [6], composing with activated carbon [7] or by doping with metals [8]. A review study on photocatalytic hydrogen production [9] has shown that the highest hydrogen productions were achieved with TiO₂ based materials doped with gold (Au), silver (Ag) or platinum (Pt) in the last 5 years. The highest hydrogen yield was determined to be 50 mmol/gcat/h with Cu₂O

sensitized TiO₂ which was trace amounts with undoped TiO₂ [6]. Transition or noble metals are widely used as electron sinks to increase the rate of reduction of H⁺ to H₂ (g) [10-13].

Recent studies indicate that rare earth (RE) doping can enhance the visible light absorption of TiO₂ and increase the photocatalytic hydrogen production activity via phase structure tuning [14-17]. There are few studies in which the effect of Er doping on the photocatalytic hydrogen production activity of TiO₂ based materials was investigated. Li et al. [18] prepared a composite of Er³⁺-Y₃Al₅O₁₂/Pt-TiO₂ and investigated its activity in the photocatalytic hydrogen production. They found that the activity of TiO₂ was increased by adding up-conversion luminescence agent Er³⁺-Y₃Al₅O₁₂ and Pt as co-catalyst. Zalas and Laniecki [16] have shown that europium (Eu) and Er doped TiO₂ had higher hydrogen yields compared to the other RE doped TiO₂.

There are several studies in which the effect of Er doping on the photocatalytic activity of TiO₂ in the degradation of organic molecules [19-24] was investigated. These studies have shown that Er incorporation in the TiO₂ lattice increased the photocatalytic activity by decreasing the electron-hole recombination rate and increasing the adsorption of organics. However there are limited information about the location of the dopant ion in these studies. These studies also indicated that there exists an optimum Er doping level which gives the highest photocatalytic activity.

The success of nanodesign and the correct prediction of the nanostructure of these materials strictly depend on a better understanding of the location of the dopant ions in the lattice/composite structure, their solubility in the main TiO₂ phase and the interphase interactions of multiphase systems. The location of the dopant ions will affect and change the electronic

configuration, hence optical behavior, electron-hole recombination and photocatalytic activity. Limited information about the reflections of these properties on the photocatalytic hydrogen production activity of TiO₂ was reported in the previous research partially as summarized before.

In this study, Er doped TiO₂ photocatalysts were prepared by sol-gel technique. The effect of Er doping on the nanophase structure, bandgap energy and surface area of TiO₂ were determined. These powder properties were further correlated to the photocatalytic hydrogen production activity.

2. Materials and Methods

2.1. Powder Preparation

TiO₂ powders containing 0 to 1 % Er₂O₃ (on molar basis) were prepared by sol-gel technique according to the following procedure. A solution containing nitric acid (HNO₃, Merck 65%), water and predetermined amount of erbium nitrate ((Er(NO₃)₃.5H₂O Aldrich 99.9% trace metal basis) in ethanol (Merck absolute) was added dropwise to a titanium tetraisopropoxide

$$d = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (1)$$

where k is the shape constant (0.9 for spherical particles), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the selected peak and

$$x_A = \left(1 + 1.26 \frac{I_R}{I_A}\right)^{-1} \quad (2)$$

where x_A is the anatase weight fraction, I_R and I_A are the intensities of the rutile (110) and anatase (101) peaks, respectively [26]. The determination of the crystal lattice

(TTIP, Aldrich 97%)/ethanol solution under vigorous stirring at room temperature. The resulting transparent sol with TTIP:H₂O:HNO₃:EtOH molar ratios of 1:2:0.06:5.9 was stirred until complete gelation was observed. The obtained gel was dried at 40°C overnight prior to heat treatment at 700°C for 3 hours.

2.2. Characterization of the powders

Phase characterization of the powders was performed by Philips X'pert Pro X-ray Diffraction (XRD) equipment with monochromated high-intensity ($\lambda=1.54\text{\AA}$) CuK α radiation by using the JCPDS cards for anatase (#84-1286) and rutile (#87-0920). The scanning rate was set as 2.5 2 θ /min between 5 and 80° with 0.033° step size. Characterization was conducted with 1-2 g powder pressed in an aluminum cassette which was also used as reference material to calculate the accurate peak positions. The crystallite sizes were calculated from the broadening of the (101) reflection for anatase and (110) reflection for rutile using Scherrer's (Sch) equation:

θ is the Bragg's angle of diffraction [25]. The rutile and anatase weight fractions were determined from the following relation:

constants for tetragonal geometry (a and c) was conducted using the following expression:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (3)$$

where d_{hkl} is the interplane distance and hkl are the Miller (plane) indices. The lattice

constants were determined by selecting two peaks (101 and 200 peaks for anatase) [27]. Lattice strain in the TiO₂ crystal lattice and

the crystallite size were calculated by using Williamson-Hall (W-H) plot with at least 4

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{\sigma} + \frac{\eta \sin \theta}{\lambda} \quad (4)$$

where σ is the effective particle size and η is the effective strain [27]. Nitrogen adsorption and desorption isotherms and surface areas were obtained with Micromeritics Gemini V surface area analyzer. UV-VIS Diffuse Reflectance Spectra (DRS) of the prepared powders were recorded by Perkin Elmer Lambda 25 equipped with an Integrating

diffraction peaks to be used in the relation:

Sphere. Pellets with 1.5 cm diameter, 2-3 mm thickness were prepared by pressing the powders with a uniaxial press. BaSO₄ was used as the reference material. Bandgaps of the prepared powders were determined by using Kubelka-Munk transformation equation given below for indirect bandgap ($n=0.5$).

$$F(R) = \frac{(1-R)^n}{2R} \quad (5)$$

where R is the reflectance and $F(R)$ is Kubelka-Munk function [28]. Photoluminescence (PL) spectra of the prepared powders were recorded with Varian Cary Eclipse Fluorescence Spectrophotometer. The same pellets prepared for UV-VIS DRS experiments were used in PL experiments. Excitation wavelength was set to 285 nm and data was collected between wavelengths of 350 and 450 nm.

(High purity, 99.99%) carrier gas volumetric flow rate was 20 ml/min. Inlet, oven and detector temperatures were 200°C, 105°C and 250°C, respectively. Calibration was conducted by a gaseous mixture containing H₂ gas (REFINERY GAS TEST SAMPLE AGILENT P/N 5080-8755).

2.3. Photocatalytic hydrogen production experiments

Photocatalytic hydrogen production experiments were performed in a batch slurry photoreactor illuminated from one side with an Osram Ultravitalux 300 W UV-VIS lamp which has solar like spectrum according to the manufacturer. Photocatalyst powders (0.1 g) were dispersed in 100 ml aqueous 25% methanol (v/v) solution. The solution was purged with N₂ gas for 15 minutes prior to illumination in order to maintain anaerobic conditions in the reactor. Gas samples with 1 ml volume were taken with a gas tight syringe (Agilent, PN 5190-1535, 2.5 ml) after 2 hours of illumination. Produced hydrogen gas was identified and quantified by Agilent 7820A (Gas Chromatograph-GC) equipped with a Molecular Sieve 5A column and thermal conductivity detector (TCD). He

3. Results and Discussion

3.1. Characterization of the powders

XRD patterns, structural properties such as crystallite size, rutile weight fraction, lattice constants, lattice strain and surface area of Er doped TiO₂ powders are given in Figure 1 and Table 1. The characteristic diffraction peaks of anatase (JCPDS Card #841286) and rutile phase (JCPDS Card #870920) were identified in the XRD patterns of the prepared powders. The nanostructure of undoped TiO₂ powder was found to be composed of both rutile and anatase phase. Anatase was found to be the main phase in all doped TiO₂ powders with trace amounts of rutile phase which could be detected up to 0.5% doping level. Er₂O₃ phase was not detected in the XRD patterns of all the doped powders. The relative intensity of anatase (101) reflection peak significantly decreased, FWHM of this peak increased and rutile phase formation was hindered by increasing Er doping level. Anatase to rutile phase transformation kinetics was significantly affected by the

increasing doping level. According to Zhang et al. [29] rare earth doping inhibits the A-R phase transformation, retards the surface area reduction at high heat treatment temperatures. The decrease of rutile weight fraction and the crystallite size supports this statement. Crystallite size and rutile weight fraction significantly decreased with Er doping level as shown in Table 1. Lattice constant a was almost the same for undoped and doped powders, however doped TiO_2 powders exhibited significantly smaller lattice constant c compared to undoped TiO_2 powder. Similar results were obtained by Liang et al. [21] and Obregon et al. [23]; however there are not much information on the interpretation of the reasons for obtaining lower c values with Er doped TiO_2 when compared to undoped TiO_2 in these studies. According to the obtained results the decrease in the lattice constant c indicated that Er^{3+} ions may enter the interstitial voids of TiO_2 lattice or segregate in the grain boundaries rather than a substitutional accommodation due to the relatively larger radius of Er^{3+} ion (103 pm) than Ti^{4+} ion (68 pm). TiO_2 lattice should expand along c axis if these ions could be replaced with Ti^{4+} ions. The contraction in c direction may be due to the more electropositivity of segregated Er ions attracting more O^{2-} than Ti^{4+} ions creating oxygen deficiencies in the TiO_2 lattice. Another reason for obtaining lower lattice constant c with Er doped TiO_2 powders may be the dependency of the lattice constants on the size of the crystallites which are significantly lower than undoped TiO_2 powder.

Lattice strain of undoped TiO_2 was found to be 0.26% and increased to 0.41% at 0.25% doping level but decreased above this doping

level. Lattice strain originates from grain boundary effects in nanostructures. A negative slope in the W-H plot indicates the presence of compressive strain, while a positive slope indicates the presence of tensile strain [30]. Slope of the W-H plots of undoped/doped TiO_2 powders were calculated as positive. The higher strain of 0.25% Er doped TiO_2 may originate from the formation of a more defective structure compared to the undoped TiO_2 and the presence of lower rutile phase formation. It is well known that rutile is a more stable phase and has an ordered structure compared to anatase. The decrease in the strain beyond 0.25% doping level may be due to the presence of a solid state solubility limit for Er^{3+} ions in the interstitials of the anatase lattice and the possible formation of $\text{Er}_2\text{Ti}_2\text{O}_7$ phase [29]. This may be due to the higher concentrations of Er^{3+} ions on the grain boundaries which may lead to segregation on TiO_2 nanoparticle surface and formation of $\text{Er}_2\text{Ti}_2\text{O}_7$ phase. There are studies indicating that $\text{RE}_2\text{Ti}_2\text{O}_7$ phases can be synthesized at relatively low heat treatment temperatures like $\sim 650\text{--}700^\circ\text{C}$ [31, 32]. These studies have shown that the formation of a $\text{RE}_2\text{Ti}_2\text{O}_7$ phase at these temperatures is thermodynamically favourable. For example Shlyakhtina et al. [31] extended the heat treatment duration to 24 hours for $\text{RE}_2\text{Ti}_2\text{O}_7$ crystallites to be XRD detectible which were hardly detectible for 2 hours at 650°C . It was found that $\text{RE}_2\text{Ti}_2\text{O}_7$ was well crystallized for 680°C heat treatment temperature and 2 hours of duration. The formation of $\text{Er}_2\text{Ti}_2\text{O}_7$ phase at 0.5 and 1% Er doping level at 700°C is possible according to these studies which may not be XRD detectible.

Figure 1. XRD patterns of the powders. (*: anatase, o: rutile)

Table 1. Physical properties of the powders.

Photocatalyst	Crystallite size (nm) Sch/W-H	Rutile wt. frac. (%)	Anatase wt. frac. (%)	a (Å)	c (Å)	Lattice volume (Å ³)	Lattice strain (%)	S _{BET} (m ² /g)
undoped	45.2/46.2	69.09	30.91	3.78	9.59	137.1	0.261	2
0.25Er	22.8/25.6	0.64	99.36	3.78	9.45	134.6	0.408	46
0.5Er	18.1/19.1	Trace	~100	3.78	9.47	134.9	0.36	54
1Er	14.7/13.5	0	100	3.77	9.41	134.1	0.276	74

UV-VIS DRS spectra and bandgap energies of Er doped TiO₂ powders are shown in Figure 2. Er doping significantly affects the UV-VIS light absorption properties of TiO₂. The spectra of Er doped TiO₂ showed a blue shift (shift to lower wavelengths) in the absorption range of TiO₂. Undoped TiO₂ would exhibit a bandgap energy between that of anatase (3.2 eV) and rutile (3.0 eV) since XRD results showed that undoped TiO₂ is composed of anatase and rutile phases. The bandgap of Er doped TiO₂ would also vary between these values depending on the doping level since Er doping level significantly affects the phase composition. The calculated direct bandgap of undoped TiO₂ is 3.08 eV and bandgaps of doped powders vary between 3.18 and 3.27

depending on the Er doping level. These results supported the XRD results which indicated that Er ions may segregate forming a new Er-Ti oxide phase on the grain boundaries or locate in the interstitial voids since bandgap energy of TiO₂ should decrease if Er ions could enter TiO₂ lattice substitutionally. Blue-shift in the bandgap does not always signify a decrease in the visible light absorption, since there are several absorption bands in the visible region as shown in the figure. Large absorption bands at the wavelengths of 452, 490, 522, 654 nm are the characteristic absorption bands of Er³⁺ ion resulting from 4f-4f transitions and the intensity of these bands increased with increasing Er doping level.

Figure 2. UV-VIS DR spectra and bandgap energies of the powders.

Information about surface oxygen vacancies and electron-hole recombination rates can be obtained by the interpretation of a PL spectrum. According to Jagdale et al. [33] the PL intensity of TiO_2 decreased with nitrogen (N) doping due to the oxygen vacancies and defects in the nanostructure of TiO_2 created by N doping. They mentioned that trapping of photogenerated electrons by the oxygen vacancies accompanied by the trapping of holes by the dopant ions or the electron transfer from the valence band to the defects with an energy level closed to the conduction band formed by the dopant ions may be the reasons for PL intensity decrease. The same phenomena was also observed when TiO_2 was doped with Cu^{2+} [34] and In^{3+} [35]. Thus the decrease in the PL intensity may be an indication of increasing number of oxygen vacancies or defects created by the introduction of dopant ions in the TiO_2 lattice. PL spectra of the powders are given in Figure 3. PL spectra of the powders were well fitted with 4 gaussian peaks at 363, 380, 394, 418 nm. Emission band from 350-400 nm

(3.55–3.1 eV) corresponds to direct electron-hole radiative recombination determined by the bandgap and emission band from 400 to 500 nm (3.1-2.48 eV) corresponds to indirect bandgap and surface recombination processes (self-trapped excitons localized on TiO_6 octahedral and oxygen vacancies on the surface of TiO_2 [36]. Undoped and doped TiO_2 have similar PL spectra which indicates that Er doping did not give rise to a new PL phenomena, however the PL spectrum of TiO_2 was affected by the Er ions in the nanostructure. Er has a stable chemical state with half or full filled electronic configuration, thus Er cannot capture electrons. Er doping can alter the PL spectrum by utilizing the surface structure by means of defects and oxygen vacancies [37]. It is known that surface oxygen vacancies can enhance the photocatalytic activity by triggering the formation of reactive free radicals. The lower intensities of the peak at 394 nm showed that the number of oxygen vacancies or defects on the grain boundaries of TiO_2 was higher for 0.5% Er doped and undoped TiO_2 compared to 0.25

and 1% Er doped TiO₂ powders.

Figure 3. PL spectra of the powders.

3.2. Photocatalytic hydrogen production activities of the powders

Photocatalytic hydrogen production activities of the prepared powders are given in Figure 4. Hydrogen yields per weight (g) and surface area (m²) of the photocatalysts were given in the left y-axis and surface areas of the photocatalysts were given in the right y-axis of the figure, respectively. Hydrogen yield per weight of the photocatalyst with undoped TiO₂ was increased by Er doping at all doping levels, on the other hand undoped TiO₂ produced more hydrogen per surface area when compared to 0.25 and 1% Er doped TiO₂. The highest hydrogen yields (on both weight and surface area basis) were obtained with 0.5% Er doped TiO₂ powder as seen in the figure.

Phase nanostructure and composition most likely is the main reason for the observed higher activities at relatively low doping levels. As mentioned in the phase structure analysis, Er ions may segregate in the grain

boundaries due to a possible solid state solubility limit and inhibit anatase to rutile phase transformation. Anatase-rutile ratio may affect the photocatalytic activity since anatase was known to exhibit higher photocatalytic activity than rutile. Increased anatase weight fraction due to Er doping may have increased the photocatalytic hydrogen production activity. Oxygen vacancies and defects formed by Er doping may also be responsible for the increase in the photocatalytic activity since oxygen vacancies or defects can serve as domains for charge carrier separation and decrease the recombination rate of electron-hole pairs. Absorption bands in the visible light region were also introduced by Er doping and the intensities of the bands were the highest for 1% doping level, however at this doping level the activity per surface area was the lowest. Formation of Er oxide particles on TiO₂ grain boundaries due to a possible solid state solubility limit of Er³⁺ ions in the anatase lattice may have decreased the photocatalytic hydrogen production activity at this doping level by blocking the reactive surface of anatase TiO₂. Rare earth ions can

interact with methanol (Lewis base) as Lewis acid due to their partial unoccupied 4f atomic orbitals [38]. The enhancement of hydrogen production activity by Er doping may also originate from the increased adsorption of methanol (sacrificial electron donor) due to this interaction.

According to Zheng et al. [24] the photogenerated electrons and holes can be efficiently separated by the presence of an optimum RE doping level. The electrical charges are redistributed with the contact of a semiconductor and another phase (solid, liquid or gas) and a double layer is formed. A space charge layer is created by the transfer of photogenerated charge carriers between these phases [39]. The space charge layer width has a lower limit for the efficient separation of photogenerated electrons and holes by the electrical field. This layer is

responsible for the separation of photogenerated electron-hole pairs. The space charge layer becomes narrower due to the increase in the surface barrier with the increasing doping level; however at very high doping levels the space charge layer becomes significantly narrower, the penetration depth of light in TiO_2 exceeds this layer and the rate of separation of photogenerated electrons and holes decreases [24]. The results of this study indicated that optimum thickness of surface barrier may be obtained with 0.5% Er doping level leading to the highest hydrogen yield.

It can be concluded that optimum nanophase structure, optical properties and high surface area showed complementary effects on the increased photocatalytic hydrogen production activity of 0.5% Er doped TiO_2 powder.

Figure 4. Photocatalytic hydrogen production activities of the powders.

4. Conclusions

In this study Er doped TiO_2 powders were prepared by sol-gel technique. Photocatalytic hydrogen production activities of the prepared powders were investigated in the presence of methanol as sacrificial electron donor. XRD, UV-VIS DRS, PL and N_2 adsorption-desorption analysis were carried out. The results have shown that photocatalyst with the optimum nanophase structure, optical and physical properties was obtained with 0.5% Er doping. The highest photocatalytic hydrogen production activity was achieved at this doping level which was attributed to the optimum anatase weight fraction, enhanced visible light absorption and decreased charge carrier recombination rate. The results of this work indicate that the nanodesign of the phase and electronic structure of TiO_2 powders can be achieved by using dopants at an optimum level for the preparation of photocatalytic materials with high hydrogen production activities.

5. Acknowledgement

This study was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) within the context of MAG-ARDEB 110M739 project.

6. References

- [1] Izumi Y. Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond. *Coord Chem Rev* 2013; 257: 171-186.
- [2] Fujishima A, Honda K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 1972; 238: 37-38.
- [3] Choudhury B, Borah B, Choudhury A. Extending Photocatalytic Activity of TiO_2 Nanoparticles to Visible Region of Illumination by Doping of Cerium. *Photochem Photobiol* 2012; 88: 257-264.
- [4] Ni M, Leung MKH, Leung DYC, Sumathy K. A review and recent developments in photocatalytic water-splitting using for hydrogen production. *Renew Sust Energ Rev* 2007; 11: 401-425.
- [5] Bashir S, Wahab AK, Idriss H. Synergism and photocatalytic water splitting to hydrogen over M/ TiO_2 catalysts: Effect of initial particle size of TiO_2 . *Catal Today* 2015; 240, Part B: 242-247.
- [6] Praveen Kumar D, Lakshmana Reddy N, Mamatha Kumari M, Srinivas B, Durga Kumari V, Sreedhar B, Roddatis V, Bondarchuk O, Karthik M, Neppolian B, Shankar MV. Cu_2O -sensitized TiO_2 nanorods with nanocavities for highly efficient photocatalytic hydrogen production under solar irradiation. *Sol Energy Mater Sol Cells* 2015; 136: 157-166.
- [7] Su E-C, Huang B-S, Liu C-C, Wey M-Y. Photocatalytic conversion of simulated EDTA wastewater to hydrogen by pH-resistant Pt/ TiO_2 -activated carbon photocatalysts. *Renew Energ* 2015; 75: 266-271.
- [8] Wang Q, Yun G, An N, Shi Y, Fan J, Huang H, Su B. The enhanced photocatalytic activity of Zn^{2+} doped TiO_2 for hydrogen generation under artificial sunlight irradiation prepared by sol-gel method. *J Sol-Gel Sci Technol* 2015; 73: 341-349.
- [9] Ahmad H, Kamarudin SK, Minggu LJ, Kassim M. Hydrogen from photocatalytic water splitting process: A review. *Renew Sust Energ Rev* 2015; 43: 599-610.
- [10] Rosseler O, Shankar MV, Du MK-L, Schmidlin L, Keller N, Keller V. Solar light photocatalytic hydrogen production from water over Pt and Au/ TiO_2 (anatase/rutile) photocatalysts: Influence of noble metal and porogen promotion. *J Catal* 2010; 269: 179-190.

- [11] Sordello F, Minero C. Photocatalytic hydrogen production on Pt-loaded TiO₂ inverse opals. *Appl Catal B-Environ* 2015; 163: 452-458.
- [12] Zou J-J, He H, Cui L, Du H-Y. Highly efficient photocatalyst for hydrogen generation prepared by a cold plasma method. *Int J Hydrogen Energy* 2007; 32: 1762-1770.
- [13] Tian H, Zhang XL, Scott J, Ng C, Amal R. TiO₂-supported copper nanoparticles prepared via ion exchange for photocatalytic hydrogen production. *J Mater Chem A* 2014; 2: 6432-6438.
- [14] Asal S, Saif M, Hafez H, Mozia S, Heciak A, Moszyński D, Abdel-Mottaleb MSA. Photocatalytic generation of useful hydrocarbons and hydrogen from acetic acid in the presence of lanthanide modified TiO₂. *Int J Hydrogen Energy* 2011; 36: 6529-6537.
- [15] Puskelova J, Michal R, Caplovicova M, Antoniadou M, Caplovic L, Plesch G, Lianos P. Hydrogen production by photocatalytic ethanol reforming using Eu- and S-doped anatase. *Appl Surf Sci* 2014; 305: 665-669.
- [16] Zalas M, Laniecki M. Photocatalytic hydrogen generation over lanthanides-doped titania. *Sol Energy Mater Sol Cells* 2005; 89: 287-296.
- [17] Zhang J, Yan S, Zhao S, Xu Q, Li C. Photocatalytic activity for H₂ evolution of TiO₂ with tuned surface crystalline phase. *Appl Surf Sci* 2013; 280: 304-311.
- [18] Li Y, Guo Y, Li S, Li Y, Wang J. Efficient visible-light photocatalytic hydrogen evolution over platinum supported titanium dioxide nanocomposites coating up-conversion luminescence agent (Er³⁺:Y₃Al₅O₁₂/Pt-TiO₂). *Int J Hydrogen Energy* 2015; 40: 2132-2140.
- [19] Castañeda-Contreras J, Marañón-Ruiz VF, Chiu-Zárate R, Pérez-Ladrón de Guevara H, Rodríguez R, Michel-Urbe C. Photocatalytic activity of erbium-doped TiO₂ nanoparticles immobilized in macro-porous silica films. *Mater Res Bull* 2012; 47: 290-295.
- [20] Lee DY, Lee M-H, Cho N-I. Preparation and photocatalytic degradation of erbium doped titanium dioxide nanorods. *Curr Appl Phys* 2012; 12: 1229-1233.
- [21] Liang C-H, Hou M-F, Zhou S-G, Li F-B, Liu C-S, Liu T-X, Gao Y-X, Wang X-G, Lü J-L. The effect of erbium on the adsorption and photodegradation of orange I in aqueous Er³⁺-TiO₂ suspension. *J Hazard Mater* 2006; 138: 471-478.
- [22] Li Y, Wang Y, Kong J, Wang J. Synthesis and photocatalytic activity of TiO₂ nanotubes co-doped by erbium ions. *Appl Surf Sci* 2015; 328: 115-119.
- [23] Obregón S, Kubacka A, Fernández-García M, Colón G. High-performance Er³⁺-TiO₂ system: Dual up-conversion and electronic role of the lanthanide. *J Catal* 2013; 299: 298-306.
- [24] Zheng Y, Wang W. Electrospun nanofibers of Er³⁺-doped TiO₂ with photocatalytic activity beyond the absorption edge. *J Solid State Chem* 2014; 210: 206-212.
- [25] Sun Z, Hu Z, Yan Y, Zheng S. Effect of preparation conditions on the characteristics and photocatalytic activity of TiO₂/purified diatomite composite photocatalysts. *Appl Surf Sci* 2014; 314: 251-259.
- [26] Spurr RA, Myers H. Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer. *Anal Chem* 1957; 29: 760-762.
- [27] Tripathi AK, Singh MK, Mathpal MC, Mishra SK, Agarwal A. Study of structural transformation in TiO₂ nanoparticles and its optical properties. *J Alloys Compd* 2013; 549: 114-120.
- [28] López R, Gómez R. Band-gap energy estimation from diffuse reflectance measurements on sol-gel and commercial TiO₂: a comparative study. *J Sol-Gel Sci Technol* 2012; 61: 1-7.

- [29] Zhang Y, Zhang H, Xu Y, Wang Y. Significant effect of lanthanide doping on the texture and properties of nanocrystalline mesoporous TiO_2 . *J Solid State Chem* 2004; 177: 3490-3498.
- [30] Maurya A, Chauhan P, Mishra SK, Srivastava RK. Structural, optical and charge transport study of rutile TiO_2 nanocrystals at two calcination temperatures. *J Alloys Compd* 2011; 509: 8433-8440.
- [31] Shlyakhtina AV, Shcherbakova LG, Knotko AV, Steblevskii AV. Study of the fluorite–pyrochlore–fluorite phase transitions in $\text{Ln}_2\text{Ti}_2\text{O}_7$ ($\text{Ln}=\text{Lu}, \text{Yb}, \text{Tm}$). *J Solid State Electrochem* 2004; 8: 661-667.
- [32] Zhang W, Zhang L, Zhong H, Lu L, Yang X, Wang X. Synthesis and characterization of ultrafine $\text{Ln}_2\text{Ti}_2\text{O}_7$ ($\text{Ln}=\text{Sm}, \text{Gd}, \text{Dy}, \text{Er}$) pyrochlore oxides by stearic acid method. *Mater Charact* 2010; 61: 154-158.
- [33] Jagadale TC, Takale SP, Sonawane RS, Joshi HM, Patil SI, Kale BB, Ogale SB. N-Doped TiO_2 Nanoparticle Based Visible Light Photocatalyst by Modified Peroxide Sol–Gel Method. *The J Phys Chem C* 2008; 112: 14595-14602.
- [34] Choudhury B, Dey M, Choudhury A. Shallow and deep trap emission and luminescence quenching of TiO_2 nanoparticles on Cu doping. *Appl Nanosci* 2014; 4: 499-506.
- [35] Wang E, Yang W, Cao Y. Unique Surface Chemical Species on Indium Doped TiO_2 and Their Effect on the Visible Light Photocatalytic Activity. *J Phys Chem C* 2009; 113: 20912-20917.
- [36] Xia X, Xiao-Yan S, Xiao-Lin G, Fang J, Ya-Jun W, Chun-Ming L, Xiao-Tao Z. Effect of N-Doping on Absorption and Luminescence of Anatase TiO_2 Films. *Chin Phys Lett* 2012; 29: 027801.
- [37] Liqiang J, Yichun Q, Baiqi W, Shudan L, Baojiang J, Libin Y, Wei F, Honggang F, Jiazhong S. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Sol Energy Mater Sol Cells* 2006; 90: 1773-1787.
- [38] Reszczyńska J, Grzyb T, Sobczak JW, Lisowski W, Gazda M, Ohtani B, Zaleska A. Visible light activity of rare earth metal doped (Er^{3+} , Yb^{3+} or $\text{Er}^{3+}/\text{Yb}^{3+}$) titania photocatalysts. *Appl Catal B-Environ* 2015; 163: 40-49.
- [39] Linsebigler A, Lu G, Yates J. Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chem Rev* 1995; 95: 735-758.