Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 5091–5095

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

$La(OH)_3$:Ln^{3+} (Ln = Sm, Er, Gd, Dy, and Eu) nanorods synthesized by a facile hydrothermal method and their enhanced photocatalytic degradation of Congo red in the aqueous solution

Yan Wang[a], Shuyang Liu[a], Yun Cai[a], Shaojuan Deng[a], Bingqian Han[a], Rong Han[a], Qing Li[a], Yude Wang[a,b,*]

[a]Department of Materials Science and Engineering, Yunnan University, 650091 Kunming, People's Republic of China
[b]State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 21 August 2013; received in revised form 23 August 2013; accepted 26 September 2013
Available online 3 October 2013

Abstract

The stable and crystalline phase Ln (Ln = Sm, Er, Gd, Dy, and Eu) doped $La(OH)_3$ ($La(OH)_3$:Ln^{3+}) nanorods were synthesized by a facile hydrothermal method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to examine the microstructure and morphology. The analysis reveals that the obtained compounds are one-dimensional (1D) rod-like nanostructures. The photodegradation of $La(OH)_3$:Ln^{3+} nanorods was tested by measuring the degradation of azo dye Congo red (CR). The experiments demonstrated that $La(OH)_3$:Ln^{3+} nanorods degraded CR much faster than undoped $La(OH)_3$ nanorods and the photodegradation efficiency of $La(OH)_3$:Ln^{3+} nanorods was significantly higher than that of undoped $La(OH)_3$ nanorods.

Keywords: Nanocrystalline materials; $La(OH)_3$; Doping; Congo red; Photocatalytic degradation

1. Introduction

Lanthanum, the lightest element in the lanthanide series, has been widely studied in its oxide, hydroxide, phosphate, or oxychloride forms and extensively applied in optoelectronic devices [1], phosphors [2], solid electrolyte [3], catalytic [4], sorbent [5], and gas sensor [6]. Especially, lanthanum hydroxide ($La(OH)_3$) is one of the novel rare earth compounds, and has been used in many field, such as ceramic, superconductive materials, hydrogen storage materials, electrode materials, etc., especially catalyst and sorbent materials [7]. From the point of view of the optical properties, comparing many reported nanostructures synthesized using various routes, little work has been carried out to investigate their photocatalytic behavior. As for optical properties of $Ln(OH)_3$ nanostructures, the photocatalytic activity are actually one of the most notable findings after following photovoltaic response. Consequently, additional studies are warranted in order to gain a better understanding of the factors governing the photoactivity of $Ln(OH)_3$ nanostructures.

Congo red [1-naphthalene sulfonic acid, 3,30-(4,40-biphenylenebis (azo)) bis (4-amino-)disodium salt] with two azo bonds (−N=N−) chromophores in its molecular structure is a well-known class of azo dyes that are of high toxicity and even carcinogenic to the animals and human and they are not readily degradable. CR from textile and dyeing industries is causing severe environmental problems and has been banned in many countries because of health concerns. However, the traditional physical, chemical and biological means of wastewater treatment often have little degradation effect on this anionic secondary diazo dye pollutant due to their complex aromatic structures, which provide them with physicochemical, thermal and optical stability [8]. Compared with the conventional

---

*Corresponding author at: Department of Materials Science and Engineering, Yunnan University, 650091 Kunming, People's Republic of China. Tel.: +86 8716 503 1124; fax: +86 8716 515 3832.
E-mail address: ydwang@ynu.edu.cn (Y. Wang).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.09.119

wastewater treatment means, photodegradation has been proved to be effective for this kind of pollutions due to its strong destructive power to mineralize the pollutants into CO_2 and H_2O. To the best of our knowledge, the photocatalytic activity of $La(OH)_3$:Ln^{3+} nanorods used as the potential photocatalytic materials for photodegradation of Congo red from the aqueous solution has been reported scarcely. In this paper, Congo red dye was selected as a model dyeing pollutant to evaluate the photodegradation activity of $La(OH)_3$:Ln^{3+} nanorods. The photodegradation activity of $La(OH)_3$ nanorods is enhanced using Ln doping.

2. Experimental

All chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification.

$La(OH)_3$:Ln^{3+} nanorods were synthesized by a facile hydrothermal method starting with corresponding rare-earth chloride hexahydrate $LnCl_3 \cdot 6H_2O$, ammonia $NH_3 \cdot H_2O$ and cationic surfactant cetyltrimethylammonium bromide (CTAB). In a typical process, the synthetic procedures were as follows: CTAB was mixed with distilled deionized water under vigorous stirring until a homogeneous solution (0.003 M) was obtained. The solution of diluted $NH_3 \cdot H_2O$ (25 wt% solution, 40 ml) was added into the CTAB solution again under vigorous stirring for 30 min. When the reaction solution became homogeneous, the aqueous solutions of corresponding $LaCl_3 \cdot 6H_2O$ (0.004 M) and $LnCl_3 \cdot 6H_2O$ (Ln = Sm, Er, Gd, Dy, and Eu) with the different Ln compositions in the range of 2.5–20 at% were added into the mixture. After stirring for 2 h, the products were severally transferred to the autoclaves, followed by sealing and heating the autoclaves at 200 °C for 4 h, respectively. After the elapsed reaction time, the autoclaves were taken out from the oven and left to cool-down spontaneously to the room temperature. The resulting products were filtered, washed with distilled water to remove surfactant CTAB, and then dried in vacuum.

Powder X-ray diffraction (XRD) characterization was carried out with Rigaku D/max-RB diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images were recorded with XL30ESEM-TMP microscope.

Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, molecular weight: 696.67 g mol^{-1}, from Guangzhou Reagent Corporation, China) was used as a model dye to investigate the photodegradation activity of $La(OH)_3$:Ln^{3+} nanorods. The degradation was carried

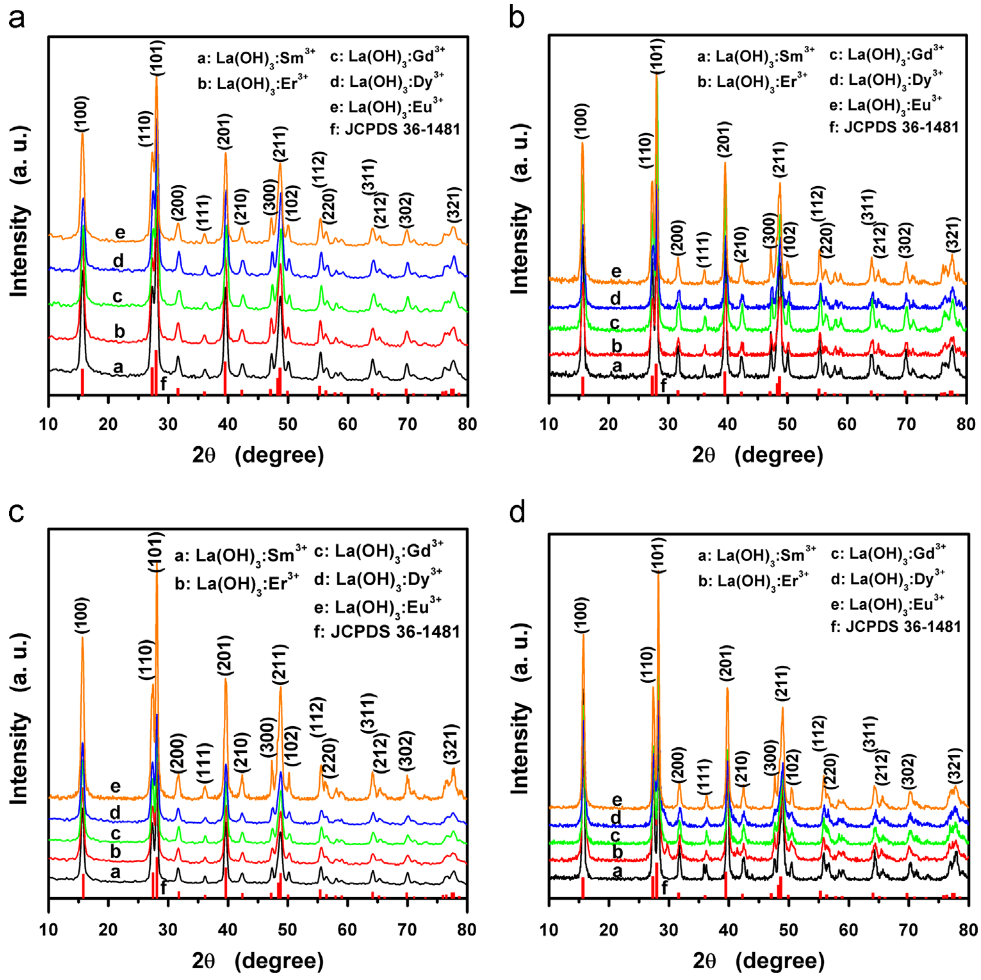

Fig. 1. XRD patterns of $La(OH)_3$:Ln^{3+} nanorods with the different doping concentration (A) 2.5%, (B) 5%, (C) 10%, and (D) 20%, respectively.

out in an aqueous solution at ambient temperature using La $(OH)_3$:Ln^{3+} nanorods as catalysts. 50 mg of the $La(OH)_3$:Ln^{3+} nanorods were added into 50 mL of CR aqueous solution with a concentration of 30 mg/L in a quartz beaker, respectively. The reaction mixtures were irradiated by a Xe-lamp (30 W) with the wavelength range of 320–400 nm in which a peak wavelength of 365 nm for UV light and 400–800 nm for visible light, and magnetically stirred throughout the photocatalytic experiment under air. The distance between the Xe-lamp and the solution surface is 8 cm. During irradiation, 4 mL of the dispersion was continually extracted at given time and subsequently centrifuged to separate catalyst and dye solutions at 4000 rpm for 30 min. The concentration (C) of the centrifuged solution and the initial concentration (C_o) of CR solution were monitored immediately by measuring the absorbance of the different supernatant at maximum absorption wavelength of 498 nm using the absorbance model by a spectrophotometer (model no. JH722N). The removal rate of CR dye was calculated using the relation of $R=((C_0-C)/C_0)\times 100\%$.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the $La(OH)_3$:Ln^{3+} nanorods. From the diffraction peaks presented in the figure, it can be confirmed that the obtained samples have polycrystalline structures, and are perfectly indexed to the hexagonal crystals of $La(OH)_3$ [space group: $P6_3/m$ (176)] in a

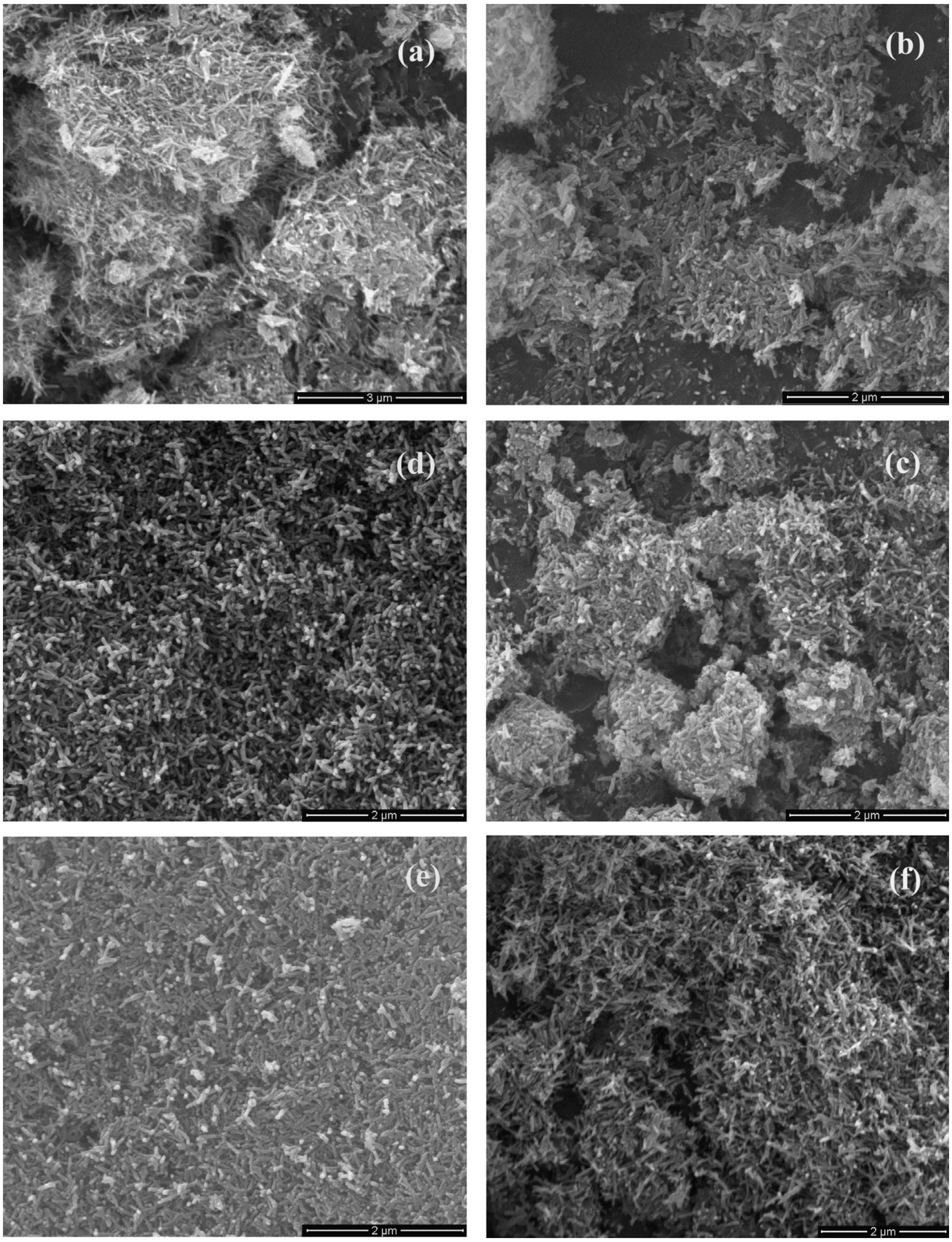

Fig. 2. SEM images of $La(OH)_3$:Ln^{3+} nanorods with a doping concentration of 20%: (a) $La(OH)_3$, (b) $La(OH)_3$:Sm^{3+}, (c) $La(OH)_3$:Er^{3+}, (d)$La(OH)_3$:Gd^{3+}, (e) $La(OH)_3$:Dy^{3+} and (f) $La(OH)_3$:Eu^{3+}.

good agreement with the values in the corresponding JCPDS cards (ICDD PDF No. 36-1481, $a=6.528$ Å, $c=3.858$ Å). Within the XRD detection limit, no secondary phases related to hydroxides or oxides of Ln are detected, indicating that the Ln doping does not change the hexagonal structure of $La(OH)_3$. It implies that the Ln^{3+} doping most probably occurs by substituting lanthanum atom in the crystal structure.

The morphology of the $La(OH)_3:Ln^{3+}$ products with doping 20% Ln^{3+} was characterized by SEM. Fig. 2 gives the images of $La(OH)_3:Ln^{3+}$, in which the nanorods are mainly composed of uniform short nanorods with diameters of about 10 nm and lengths of 100–150 nm. No particles can be observed in the sample. SEM observation reveals that they all exhibit one-dimensional rod-like nanostructures and have high aspect ratio.

The synthetic $La(OH)_3:Ln^{3+}$ nanorods with a defined structure offer an opportunity to investigate the crystal size/surface-dependent photocatalytic properties for organic pollutants in an aqueous solution. The results of degradation experiments (Fig. 3) show that Congo red can be effectively removed by the $La(OH)_3:Ln^{3+}$ nanorods. Rapid removal of CR is observed at the beginning of the reaction time. Following the rapid removal, the removal rate decreased, and an apparent equilibrium is reached after several hundred or more than ten hundred minutes depending on the different Ln^{3+} doping. It is found that $La(OH)_3:Ln^{3+}$ nanorods degrade CR much faster than undoped $La(OH)_3$ nanorods. The as-synthesized $La(OH)_3:Ln^{3+}$ nanorods exhibit higher photodegradation activity compared with pure $La(OH)_3$ nanordos. It can also be seen that the as-synthesized $La(OH)_3:Ln^{3+}$ nanorods with a Ln content of 20 mol% show the highest photodegradation activity. Furthermore, photodegradation activity of the $La(OH)_3:Ln^{3+}$ nanorods increases gradually with an increase of the Ln doping content.

The photocatalytic activity of semiconductor is based on the generation of electron (e^-)–hole (h^+) pair upon light irradiation, and thus the photocatalytic efficiency depends on two processes: one is the competition between the recombination and capture of photogenerated electrons and holes; the other is the competition between the recombination of captured electrons and holes and interface charge transfer. In our case, the proposed impurity level and the lattice defects, which can effectively enhance the electron–hole separation rate in $La(OH)_3$ nanorods, are generated in the presence of the singly oxygen vacancy (V_O^+) defects in the as-synthesized pure $La(OH)_3$. V_O^+ defect can easily work as electron donors to form charged oxygen vacancy (V_O^{++}) [9] and simultaneously trap the photogenerated holes temporarily to reduce the surface recombination of electrons and holes [10]. It can be deduced that the more the singly ionized oxygen vacancy (V_O^+) defects,

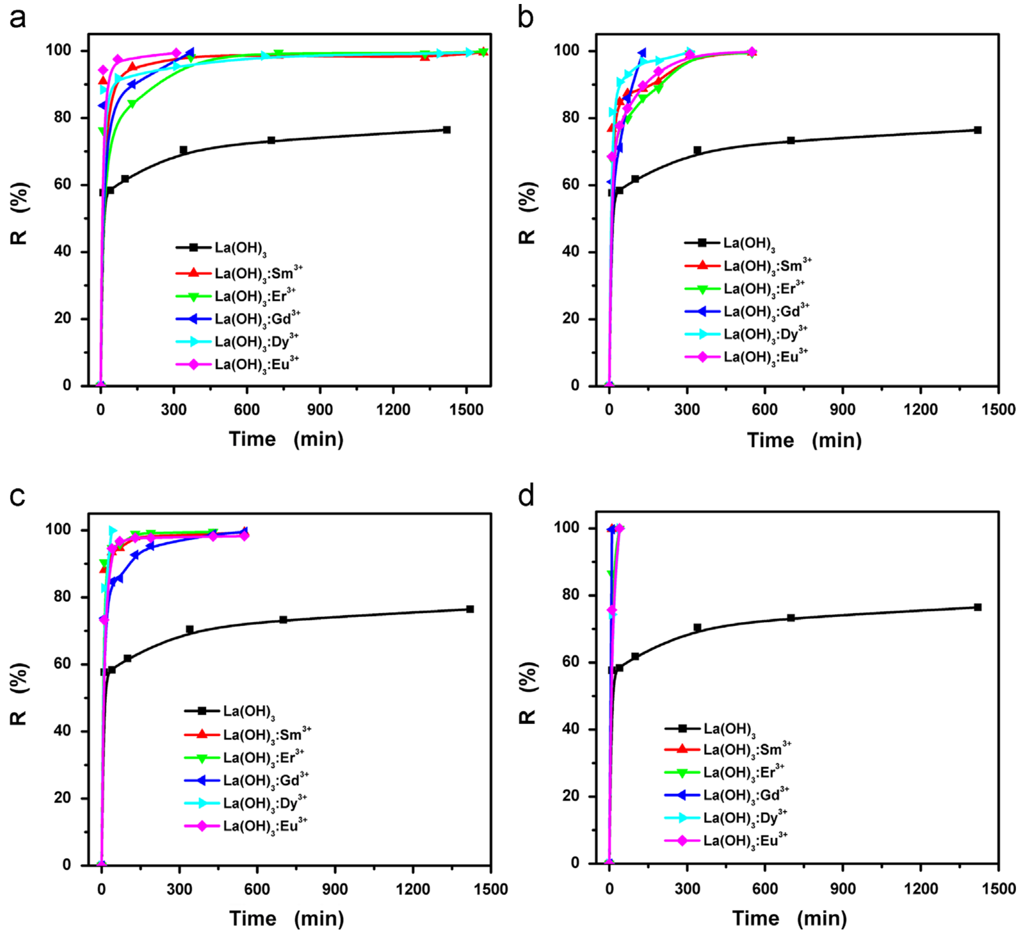

Fig. 3. Photodegradation activity of $La(OH)_3:Ln^{3+}$ nanorods for Congo red with the different doping concentration (a) 2.5%, (b) 5%, (c) 10%, and (d) 20%.

the higher the photodegradation activity [11]. As the XRD analysis, Ln is proposed to be located at substitutional positions instead of lanthanum substitutional site. With increase in doping concentrations of Ln, the singly ionized oxygen vacancy (V_O^+) defect concentration and the corresponding photodegradation activity of $La(OH)_3:Ln^{3+}$ increase. In most cases, h^+ can easily react with surface bound H_2O to produce $\cdot OH$ radicals. It is well known that the OH radical is a powerful oxidizing agent capable of degrading most pollutants. The CR dye can be photoxidated by OH in deep level, and then be degraded to form smaller organic molecules, and these organic molecules can eventually be mineralized into CO_2 and H_2O. Based on these findings, the possible degradation mechanism of Congo red in the presence of $La(OH)_3:Ln^{3+}$ nanorods can be proposed as follows:

$$hv \overset{\mathrm{Ln(OH)_3:Ln^{3+}}}{\rightarrow} e^- + h^+ \tag{1}$$

$$O_2 + e^- \rightarrow \bullet O_2^- \tag{2}$$

$$CR + O_2^- \rightarrow CR_{ox}(\text{intermediates}) \rightarrow CO_2 + H_2O \tag{3}$$

$$V_O^+ + h^+ \rightarrow V_O^{++} \tag{4}$$

$$V_O^{++} + OH^- \rightarrow V_O^+ + \bullet OH \tag{5}$$

$$CR + \bullet OH \rightarrow CR_{ox}(\text{intermediates}) \rightarrow CO_2 + H_2O \tag{6}$$

4. Conclusions

The feasibility of employing Ln (Ln = Sm, Er, Gd, Dy, and Eu) doped $La(OH)_3$ nanorods for the photodegradation of CR has been demonstrated. Among the nanorods, 20 at% Ln-doped $La(OH)_3$ nanorods showed a superior performance towards degradation of CR, whereas relative low photodegradation activity was observed for undoped $La(OH)_3$ nanorods. It has been concluded that higher doping concentration and increase in the lattice defects of $La(OH)_3$ upon Ln doping have significant influence on the enhanced photocatalytic activity of $La(OH)_3:Ln^{3+}$ nanorods.

Acknowledgments

This work was supported by the Department of Science and Technology of Yunnan Province via the Key Project for the Science and Technology (Grant no. 2011FA001), the National Natural Science Foundation of China (Grant no. 51262029), and the State Key Laboratory of Silicon Materials visiting scholar Fund (Grant no. SKL2012-16).

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2013.09.119.

References

[1] A.A. Dakhel, Preparation and optical study of Au nanograins in amorphous La-oxide medium, Colloids and Surfaces A: Physicochemical and Engineering Aspects 332 (2009) 9–12.

[2] M. Ferhi, K. Horchani-Naifer, M. Férid, Hydrothermal synthesis and photoluminescence of the monophosphateLaPO4:Eu(5%), Journal of Luminescence 128 (2008) 1777–1782.

[3] N. Imanaka, K. Okamoto, G.Y. Adachi, Lanthanum oxychloride-based solid electrolytes with ultra-high chloride ion conductivity, Angewandte Chemie International Edition 41 (2002) 3890–3892.

[4] E. Ordonez-Regil, R. Drot, E. Simoni, J.J. Ehrhardt, Sorption of uranium (VI) onto lanthanum phosphates surfaces, Langmuir 18 (2002) 7977–7984.

[5] S. Tokunaga, S.A. Wasay, S.W. Park, Removal of arsenic(V) ion from aqueous solutions by lanthanum compounds, Water Science and Technology 35 (1997) 71–78.

[6] N. Imanaka, K. Okamoto, G. AdachiN, Chlorine gas sensor based on the combination of Mg^{2+} cation conducting and O^{2-} anion conducting solid electrolytes with lanthanum oxychloride as an auxiliary electrode, Electrochemistry Communications 3 (2001) 49–51.

[7] M.P. Rosynek, D.T. Magnuson, Preparation and characterization of catalytic lanthanum oxide, Journal of Catalysis 46 (1977) 402–413.

[8] Z.J. Yang, J.J. Wei, H.X. Yang, L. Liu, H. Liang, Y.Z. Yang, Mesoporous CeO_2 hollow spheres prepared by ostwald ripening and their environmental applications, European Journal of Inorganic Chemistry 2010 (2010) 3354–3359.

[9] S.Y. Liu, Y. Cai, X.Y. Cai, H. Li, F. Zhang, Q.Y. Mu, Y.J. Liu, Y.D. Wang, Catalyzed degradation Congo red in the aqueous solution by $Ln(OH)_3$ (Ln = Nd, Sm, Eu, Gd, Tb, and Dy) nanorods, Applied Catalysis A: General 453 (2013) 45–53.

[10] Y. Hu, H.J. Chen, Origin of green luminescence of ZnO powders reacted with carbon black, Journal of Applied Physics 101 (2007) 124902 (3 pages).

[11] A.B. Djurišić, Y.H. Leung, Optical properties of ZnO nanostructures, Small 2 (2006) 944–961.