

# Luminescent properties of complexes $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$ in nano-TiO<sub>2</sub>

Yuguang Lv<sup>a,b</sup>, Jingchang Zhang<sup>a,\*</sup>, Weiliang Cao<sup>a</sup>, Yali Fu<sup>a</sup>, Xia Wu<sup>a</sup>

<sup>a</sup> Institute of Modern Catalysis, Beijing University of Chemical Technology, State Key

Laboratory of Chemical Resource Engineering, Beijing 100029, China

<sup>b</sup> College of Chemistry and Pharmacy, Jiamusi University, Heilongjiang, Jiamusi 154007, China

Received 31 December 2006; received in revised form 24 July 2007; accepted 27 July 2007

Available online 11 August 2007

## Abstract

A series of HTTA (thenoyltrifluoroacetone) and TPPO (trioctylphosphine oxide) complexes with different molar ratios of Eu<sup>3+</sup> to Y<sup>3+</sup> has been synthesized. Characterization with XRD, IR, UV, elemental analysis and fluorescence spectroscopy has also been carried out. These results showed luminescence of Eu<sup>3+</sup> complex was enhanced after doped with Y<sup>3+</sup>. The organic–inorganic thin film of complexes  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$  in nano-TiO<sub>2</sub> was fabricated, and the nano-TiO<sub>2</sub> has been used in the luminescence layer to change the luminescence property of complexes  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$ . It was found that there was an efficient energy transfer process between the ligands and metal ions.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Rare earth complexes; Synthesis; Luminescent properties

## 1. Introduction

Since the 1960s, the complexes of Eu(TTA)<sub>3</sub>Phen and Sm(TTA)<sub>3</sub>Phen have attracted considerable attention because of their high fluorescence emission efficiency, which owe to high absorption coefficient of HTTA and the synergistic effect of 1, 10-phenanthroline, which are suitable to be used as the emission materials [1–4]. Therefore, many rare earth complexes have been synthesized and used as the emitters in photoluminescence and electroluminescence devices [5–10]. It is an effective method to improve the luminescence intensity of lanthanide complex by using inorganic semiconductor materials ZnS and TiO<sub>2</sub> [11–16]. However, little attention has been paid to rare earth ternary complexes with Eu<sup>3+</sup> (or Y<sup>3+</sup>), HTTA and TPPO in nano-TiO<sub>2</sub>.

The complexes of  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$  were synthesized, and nano-TiO<sub>2</sub> was mixed with the rare earth complex to form the luminescence layer in the luminescence. It was found that there was an efficient energy transfer process between the complex and europium ion. The nano-TiO<sub>2</sub> acts as an energy transfer bridge that helps energy transfer from Y<sup>3+</sup> to Eu<sup>3+</sup>. It

shows that it is an effective method to improve the luminescent intensity of lanthanide complex by using electronic characteristics of inorganic semiconductor materials.

## 2. Experimental details

### 2.1. Sample preparation

1 mmol of mixture of YCl<sub>3</sub>·6H<sub>2</sub>O and EuCl<sub>3</sub>·6H<sub>2</sub>O (mole ratios of the Eu<sup>3+</sup> to Y<sup>3+</sup> are 1.0:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, 0.1:0.9 and 0:1.0, respectively), 3 mmol of HTTA were dissolved in 30 ml ethanol. The pH value of the mixture was adjusted to 6–7 by adding 3 mmol triethylamine. TPPO in ethanol solution was added to the reaction mixture, the molar ratio of TPPO to RE<sup>3+</sup> ion being 2:1. Then, the solution was stirred for 2 h at room temperature. The precipitate was filtered, washed with water and ethanol, dried at room temperature, and then stored in a silica-gel drier. Nano-TiO<sub>2</sub> was prepared using the chemical vapor deposition (CVD) of TiCl<sub>4</sub> [17].

### 2.2. Measurements

X-ray diffraction (XRD) analysis was carried out by D/MAX 2500 VB2+/PC (Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ),  $V = 40 \text{ kV}$ ,  $I = 200.0 \text{ Ma}$ ,  $\lambda = 1.54056 \text{ \AA}$ ). Infrared spectra were recorded in the range of “4000–400 cm<sup>-1</sup>” by a prostige-21IR spectrophotometer in KBr flake. Elemental analyses were carried out by the Perkin-Elmer 240C analytical instrument. UV–vis spectra were performed on a UV-2501PCS double spectrophotometer. The excitation and emission spectra measurements were performed on a Shimadzu 5301 spectrofluorophotometer

\* Corresponding author. Tel.: +86 1 64434904; fax: +86 1 64434898.

E-mail address: zhangjc1@mail.buct.edu.cn (J. Zhang).

equipped with a 150 W xenon lamp as the excitation source. Spectra were recorded using monochromator slit widths of 1.5 nm on both excitation and emission sides. Lifetimes were measured with a Spex 1934D phosphorimeter using a 450-W flash lamp as the excitation source (pulse width = 3  $\mu$ s).

### 3. Results and discussion

#### 3.1. X-ray diffraction

We conducted an investigation into samples by XRD. From the obtained grain size and complexes XRD microstructural parameter, we found some patterns as follows: according to Scherrer formula:  $D = 0.89\lambda / (\beta \cos \theta)$ , for  $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$ , grain size  $D = 93.6 \text{ \AA}$ ;  $\text{Y}(\text{TTA})_3(\text{TPPO})_2$ ,  $D = 82.6 \text{ \AA}$ ;  $\text{Y}_{0.5}\text{Eu}_{0.5}(\text{TTA})_3(\text{TPPO})_2$ ,  $D = 81.5 \text{ \AA}$ . The average size of complexes was about 81–85  $\text{ \AA}$ . In Fig. 1, it can be seen that the pattern of complex  $\text{Y}_{0.5}\text{Eu}_{0.5}(\text{TTA})_3(\text{TPPO})_2$  is the similar to that of pure complexes, and the peaks of curve are the characteristic diffuse scattering peaks of rare earth complexes. Similar results also can be attained in other rare earth complex-doped  $\text{Y}^{3+}$ .

#### 3.2. IR spectra analysis

The obtained products were proved by FTIR spectra using KBr as the matrix material. Infrared spectra of ligands and complexes are shown in Fig. 2, ranging from 4000 to 400  $\text{cm}^{-1}$ .  $\text{Y}_{0.5}\text{Eu}_{0.5}(\text{TTA})_3(\text{TPPO})_2$ : 1650(s, C=O), 1250–1150(s, C–F), 1125(s, P=O). The IR spectra of doped complexes are obviously different from that of ligands TTA and TPPO, but are identical with  $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$  complex. This indicates that the  $\text{Y}_{1-x}\text{Eu}_x(\text{TTA})_3(\text{TPPO})_2$  complexes are similar to the complexes reported before [10]. The compositions of the complexes were confirmed by elemental analysis. Elemental analysis data of europium complex and  $\text{Y}_{1-x}\text{Eu}_x(\text{TTA})_3(\text{TPPO})_2$  ( $x = 0.5$  and 0.75, which is selected randomly) are listed in Table 1. The chemical structure of rare earth complex is shown in Fig. 3.

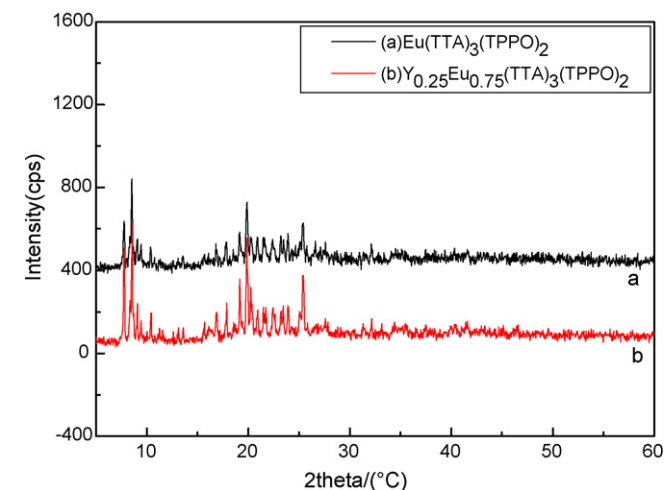


Fig. 1. XRD patterns of complexes  $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$  and  $\text{Y}_{0.25}\text{Eu}_{0.75}(\text{TTA})_3(\text{TPPO})_2$ .

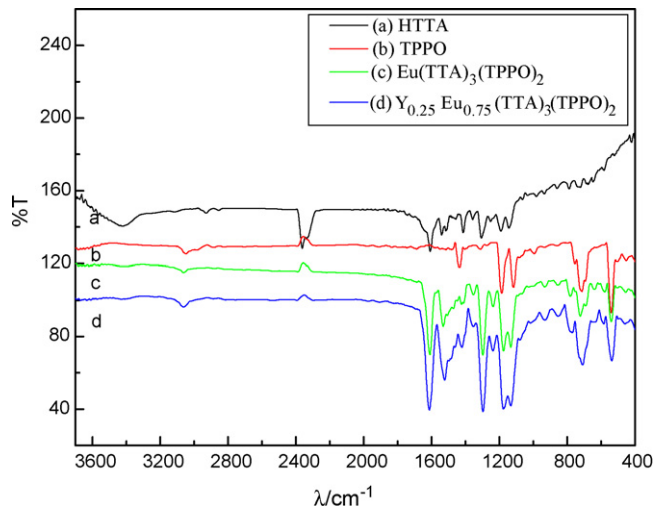


Fig. 2. Infrared spectra of TTA, TPPO and complexes: (a) TTA; (b) TPPO; (c)  $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$  and (d)  $\text{Y}_{0.5}\text{Eu}_{0.5}(\text{TTA})_3(\text{TPPO})_2$ .

Table 1  
Elemental analysis

Complex	Eu (Y) %	Analytically found (calculated) %	
		C	H
$\text{Eu}(\text{TTA})_3(\text{TPPO})_2$	11.10 (11.08)	52.53 (52.49)	3.10 (3.06)
$\text{Y}_{0.25}\text{Eu}_{0.75}(\text{TTA})_3(\text{TPPO})_2$	10.10 (10.05)	53.14 (53.10)	3.06 (3.10)
$\text{Y}_{0.5}\text{Eu}_{0.5}(\text{TTA})_3(\text{TPPO})_2$	8.87 (8.90)	53.71 (53.73)	3.16 (3.13)

#### 3.3. Fluorescence properties

All excited spectra were recorded by monitoring the  $\text{Eu}^{3+}$  fluorescence at 613 nm. Emission spectra of complexes were obtained by exciting these complexes using 375 nm ultraviolet. The excitation and emission spectra of all complexes

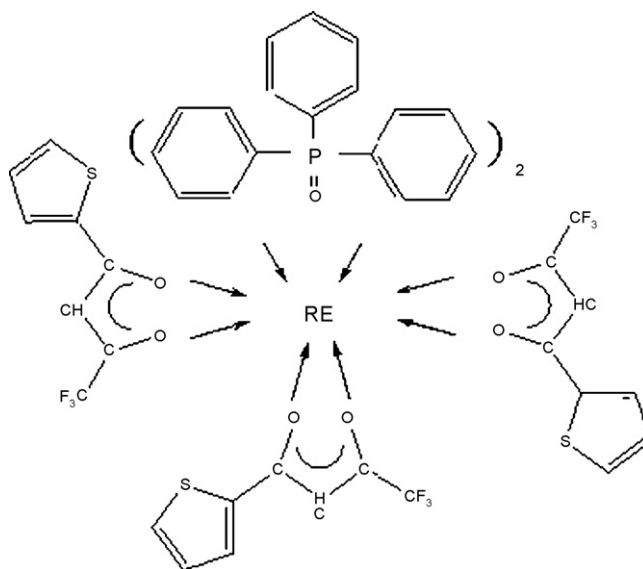


Fig. 3. The chemical structure of rare earth complexes.

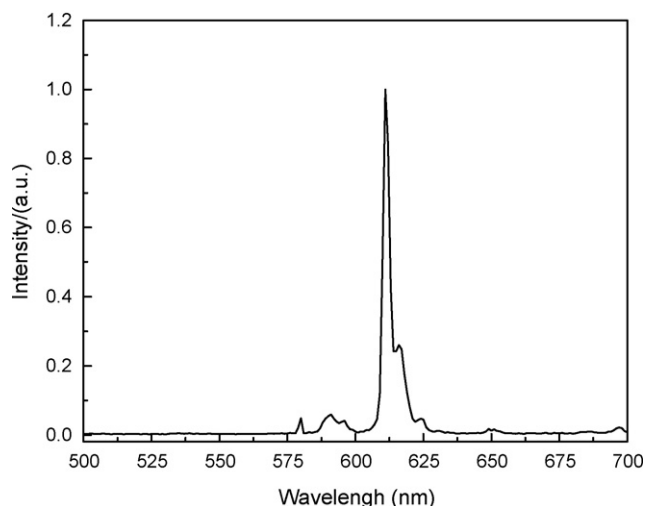


Fig. 4. Typical emission spectrum of complex  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  in  $CHCl_3$  solution ( $\lambda_{ex} = 375$  nm).

with different doping ions have the similar profile. In Fig. 4, five typical  $Eu^{3+}$  luminescence peaks appear at 583.0, 593.5, 614.0, 656.0 and 707.5 nm, which belong to  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_3$  and  $^5D_0 \rightarrow ^7F_4$ , respectively. This experimental result shows that the relative intensity of  $^5D_0 \rightarrow ^7F_2$  is the strongest, which indicates there is a typical  $Eu^{3+}$  luminescence emission. Fluorescence emissions intensity of the complexes is enhanced with an addition of  $Y^{3+}$  ions. For  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$  complex, different mole fraction of  $Y^{3+}$  have different influences on emissions intensity of doped complexes. The optimum mole fraction of doped  $Y^{3+}$  is 0.25, and the  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  has the strongest luminescence emission. Then, the intensity of  $Eu^{3+}$  complex was reduced with raising the content of the  $Y^{3+}$  ion (the result is listed in Table 2).

### 3.4. UV absorption spectra and fluorescence properties of complex in nano-M

The organic–inorganic film of  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2/nano-M$  was fabricated, the nano-M ( $M = CdS, TiO_2$  and  $TiO_2 + CdS5\%$ ) has been used in the luminescence layer to change the luminescence property of complexes of  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$ .  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$  was doped into nano-M at different weight ratio, and the thin film was fabricated on the top of glass substrate. Two kinds of struc-

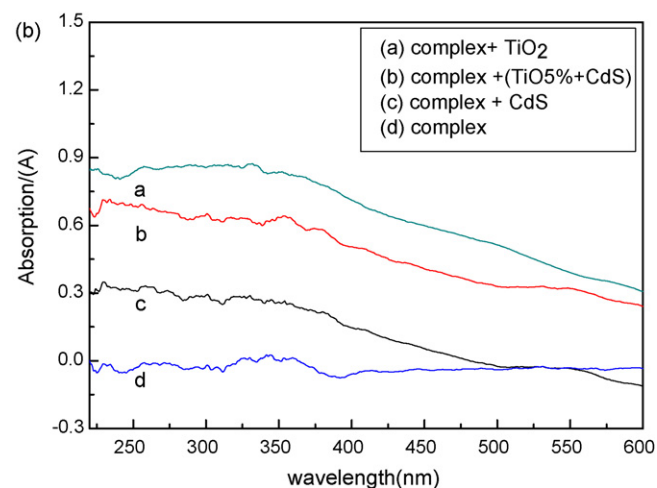
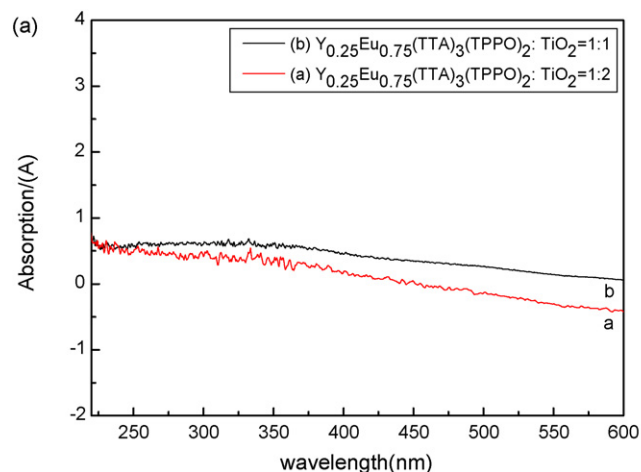


Fig. 5. (a) UV spectra of  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2/TiO_2$  in organic–inorganic thin film: (a)  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2/TiO_2 = 1:2$  and (b)  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2/TiO_2 = 1:1$ . (b) UV spectra of complexes  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  and  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2/nano-M$  (the weight ratio of nano-M: RE = 1:1 (mg)).

tural devices were fabricated and signed a symbol A and B, respectively.

The thin film A: ITO/ $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  (60 nm): nano-M (10–20 nm).

The thin film B: ITO/ $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  (60 nm).

The UV absorption spectra of the complex and complex-doped nano-M are shown in Fig. 5. It can be seen that

Table 2

The luminescence properties of rare earth complexes

Matter	$Y_{1-x}Eu_x(TTA)_3(TPPO)_2$		Relative intensities (a.u.)	Lifetimes ( $\mu s$ )
	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)		
$Y_{0.9}Eu_{0.1}(TTA)_3(TPPO)_2$	375	614	996	960
$Y_{0.75}Eu_{0.25}(TTA)_3(TPPO)_2$	375	614	1106	988
$Y_{0.5}Eu_{0.5}(TTA)_3(TPPO)_2$	375	614	1125	1018
$Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$	375	614	1538	1265
$Y_{0.1}Eu_{0.9}(TTA)_3(TPPO)_2$	375	614	966	789
$Eu(TTA)_3(TPPO)_2$	375	614	860	642

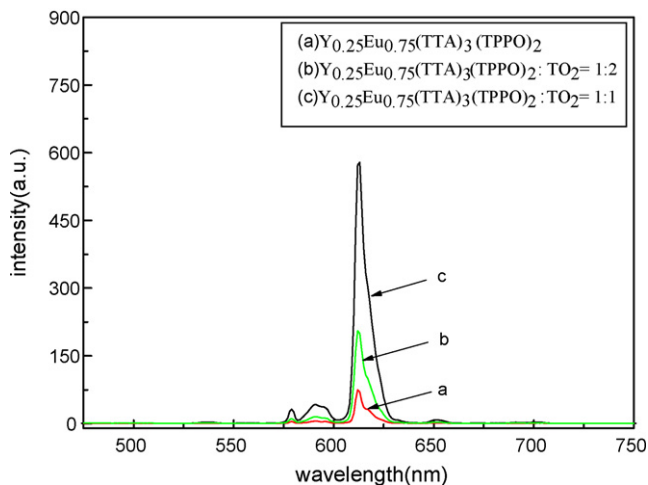


Fig. 6. Typical emission spectra of complex  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$ , the weight ratio of  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  and  $TiO_2$  is 1:1 and 2:1, respectively.

the absorption bands of complex  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$ -doped nano-M did not show significant difference in comparison with the complex  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  except that the intensity of the absorption peaks enhanced slightly. The main absorption band ranges from 220 to 600 nm, which is attributed to the  $\pi \rightarrow \pi^*$  transitions of  $TTA^-$ . The weight ratio of nano- $TiO_2$ : RE complexes = 1:1 (mg) in 1 ml DMF is the best.

Fig. 6 shows emission spectra of complex  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$ , the weight ratio of  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$  and  $TiO_2$  is 1:1 and 2:1, respectively. In the thin film A, semiconductor  $TiO_2$  thin film acts as transporting layer according to its electronic characteristics and energy level, the intensity of the red emission at 614 nm in the thin film A is stronger than the thin film B. In both structural of the thin film, the characteristic emissions of europium ions at 594, 614, 655 and 690 nm are obtained. These emission peaks are ascribed to four energy level transitions of  ${}^5D_0 \rightarrow {}^7F_J$  ( $J=1, 2, 3, 4$ ) of europium ion ( $Eu^{3+}$ ), respectively. The luminescence intensity of  ${}^5D_0 \rightarrow {}^7F_2$  is the strongest. As shown in Fig. 6, emission of  $Eu^{3+}$  is enhanced due to the introduction of  $TiO_2$ , which helps the energy transfer from ligands to  $Eu^{3+}$ . These results demonstrate an efficient energy transfer from  $Y^{3+}$  to  $Eu^{3+}$ , which exists in the complex of  $Y_{0.25}Eu_{0.75}(TTA)_3(TPPO)_2$ . Finally, most of the energy is given out by the radiation of  ${}^5D_0 \rightarrow {}^7F_2$  transition of the  $Eu^{3+}$  ion.

#### 4. Conclusion

Using co-precipitating method, a series of complexes  $Y_{1-x}Eu_x(TTA)_3(TPPO)_2$  was synthesized. This experiment

result showed that luminescence of  $Eu^{3+}$  complex was enhanced after doped with  $Y^{3+}$ . PL spectra indicate that the  $Eu^{3+}$  emission is enhanced by codoping the complexes. The  $Y^{3+}$  ion acts as an energy transfer bridge that helps energy transfer from ligands to  $Eu^{3+}$ . A novel thin film with organic-inorganic structure was fabricated, nano- $TiO_2$  was utilized as electron function layer, so the excitation of lanthanide can be carried out in a new route (which means electrons directly impact excitation of the lanthanide ions through resonant energy transfer). Thus, it can be expected that nano- $TiO_2$  material plays an important role in improving luminescent intensity of lanthanide complex.

#### Acknowledgments

This work was supported by research fund for the Doctoral Program of Higher Education (No. 20050010014), National Development Project of High Technology (Project 863) (2006AA03Z 412) and Education Commission of Hei Long Jiang Province (11521280).

#### References

- [1] J.C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, A.F. Williams, J. Am. Chem. Soc. 115 (1993) 817.
- [2] Q. Wang, B. Yan, X. Zhang, J. Photochem. Photobiol. A: Chem. 174 (2005) 119.
- [3] M. Hasegawa, A. Ishii, S. Kishi, J. Photochem. Photobiol. A: Chem. 178 (2006) 220.
- [4] H. Song, J. Wang, J. Lumin. 118 (2006) 220.
- [5] N. Murase, R. Nakamoto, J. Matsuoka, A. Tomita, J. Lumin. 107 (2004) 256.
- [6] G. Zhong, Y. Wang, C. Wang, J. Lumin. 99 (2002) 213.
- [7] K. Takato, N. Gokan, M. Kaneko, J. Photochem. Photobiol. A: Chem. 169 (2005) 109.
- [8] K.K. Mahato, S.B. Rai, A. Rai, Spectrochim. Acta Part A 60 (2004) 979.
- [9] B. Yan, H. Zhang, S. Wang, J. Ni, J. Photochem. Photobiol. A: Chem. 116 (1998) 209.
- [10] Y. Liu, C. Ye, G. Qian, J. Qiu, M. Wang, J. Lumin. 118 (2006) 158.
- [11] Y. Wang, F. Teng, Z. Xu, Y. Hou, Appl. Surf. Sci. (2004) 236.
- [12] F. Zhang, Z. Xu, F. Teng, L. Liu, L. Meng, Mater. Sci. Eng. B 123 (1) (2005) 84.
- [13] F. Zhang, Z. Xu, F. Teng, J. Lumin. 117 (2006) 90.
- [14] E. Stathatos, P. Lianos, Chem. Phys. Lett. 417 (2006) 406.
- [15] Y. Sun, H. Jiu, D. Zhang, J. Gao, B. Guo, Q. Zhang, Chem. Phys. Lett. 410 (2005) 204.
- [16] Y. Lv, J. Zhang, W. Cao, F. Zhang, Z. Xu, J. Photochem. Photobiol. A: Chem. 188 (2007) 155.
- [17] S. Pilkenton, S.-J. Hwang, D. Raftery, J. Phys. Chem. B 103 (1999) 11152.