

$\text{Eu}^{2+}/\text{Gd}^{3+}$ -codoped nanocrystalline titania catalyst and its photocatalytic activity under natural light

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Received 15 July 2007; accepted 10 September 2007

Abstract: $\text{Eu}^{2+}/\text{Gd}^{3+}$ -codoped nanocrystalline titania catalysts were prepared by a modified sol-gel method. Powder X-ray diffraction, Transmission electron microscopy and UV-Vis spectra analyse were carried out to characterize the catalysts with different $\text{Eu}^{2+}/\text{Gd}^{3+}$ contents. The photocatalytic efficiency was evaluated by the photodegradation of methyl orange in an aqueous solution under natural light irradiation. It has been confirmed that $\text{Eu}^{2+}/\text{Gd}^{3+}$ -codoped titania could be excited by natural light. The higher natural light activity is due to the codoping of $\text{Eu}^{2+}/\text{Gd}^{3+}$. An optimum synergetic effect was found for a mass ratio of Eu/TiO_2 equal to 1.0% and Gd/TiO_2 equal to 0.5%. The effects induced by $\text{Eu}^{2+}/\text{Gd}^{3+}$ -codoped on the titania catalysts may be explained in terms of $\text{Gd}^{3+}\rightarrow\text{Eu}^{2+}$ energy transfer to affect the photocatalysis activity of the titania catalysts.

Key words: titania catalysts; codoping; synergetic effect

1 Introduction

TiO_2 photocatalyst has many advantages including innocuity, high catalytic activity, strong oxidizing power, good stability, and mild reaction condition; it has high eliminating efficiency to low concentration pollutant and gaseous pollutant, it can also operate and prepare at low cost and could be used directly in sunlight, so it is an extraordinary material to control pollution. But TiO_2 photocatalyst has some disadvantages in practical usage now, for example, it has low utilizing efficiency for natural light energy, and its forbidden band is too wide that only absorbing in ultraviolet band, the combination of photoproductive electron and positive hole (express as electron/hole; e^-/h^+) results in low catalytic efficiency[1-2]. In order to increase the TiO_2 photocatalyst capability and let it be used in practice, a great deal of efforts show that doping metal ions is an effective way[3-6]; there are many papers concerning with doping single metal ion which can increase TiO_2 photocatalyst capability, but about codoping both metal ions for nanometer TiO_2 , special with rare earth, there are

only a few reports and discussion[7]. In this work, we report a new nanometer TiO_2 photocatalyst that is prepared by codoping Gd^{3+} and Eu^{2+} , and has investigated its photocatalysis activity under natural light, whose target-degraded substance is methyl orange. Meanwhile the mutual action between Gd^{3+} and Eu^{2+} and the way of how to affect the photocatalysis activity of nanometer TiO_2 are contrasted and analyzed; the advantages of codoping Gd^{3+} and Eu^{2+} are construed from the $\text{Eu}^{2+}\text{-Gd}^{3+}$ energy transfer process, in short it is a new method to use nanometer TiO_2 in practice with codoping Gd^{3+} and Eu^{2+} .

2 Experimental

2.1 Catalyst preparation

Gd^{3+} and Eu^{2+} codoped nanometer TiO_2 can be synthesized with sol-gel method[10], the preparing process is as following: mix the tetrabutyl titanate ($(\text{CH}_3(\text{CH}_2)_3\text{O})_4\text{Ti}, \text{CP}$) and absolute ethyl alcohol together according to a certain proportion, quickly drop the concentrated hydrochloric acid to above solution to adjust its pH value to approximately 3.0, then drop the

Foundation item: Project(50174024) supported by the National Natural Science Foundation of China; Project(03JJY4046) supported by the Natural Science Foundation of Hunan Province, China; Project(03C057) supported by the Scientific Research Fund of Hunan Provincial Education Department, China

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mixed solution of gadolinium nitrate and europium nitrate (obtained by dissolving gadolinium oxide and europia in concentrated nitric acid) at rate of 1/2 droplet per second; the components of mixed solution are listed in Table 1 (given as molar ratio of doping Gd^{3+} and Eu^{2+}). A transparent gel can be obtained after 2 h with stopped stirring, then dry up the gel in oven at 80–100 °C, and calcine the dried gel in muffle at 550 °C for 2 h, take out and mill it, the catalyst samples given in Table 1 are obtained with different doping ratio(molar ratio of doping); The Eu^{2+} content is fixed at 0%, 0.1%, 0.5%, 1.0%, 1.5%, and 2.0 % in series 1–6 respectively, but Gd^{3+} content changes from 0% to 2.0% in each series listed in Table 1.

2.2 Characterization

Powder X-ray diffraction (SIEMENS D5000, SIEMENS, Germany), transmission electron microscopy (JEM-2010, JEOL Company, Japan) and UV-Vis spectra analysis (UV-2100, SHIMADZU Corporation, Japan) were carried out to characterize the catalysts with different Eu^{2+}/Gd^{3+} contents.

2.3 Photodegradation experiment

The photocatalysis of codoped Gd^{3+} and Eu^{2+} nanometer TiO_2 were performed at homemade reaction system[8]. No pure oxygen and other substance except methyl orange were added in all of photocatalytic experiments. The natural light was used as light source and the methyl orange was employed as the target substance that could be degraded in the experiment. The concentration of methyl orange was 20 mg/L at the beginning; experiment was carried out at room temperature. Took out upper layer clear solution at a fixed period, separated by centrifugation at high speed,

and then took out clear solution to measure its absorbance with spectrophotometer, and calculated the degrading rate of methyl orange. The degrading rate can be used to express the photocatalysis activity of the nanometer TiO_2 [9].

3 Result and discussion

3.1 XRD and TEM analysis

XRD results show that all the samples in Table 1 are anatase. The even diameter of catalyst grain can be estimated with Scherrer formula according to full width half maximum of the furthest diffraction peak (101) in XRD pattern[10], the calculated results show that the diameter of nanometer TiO_2 changes only with total doping metal mass and decreases with increasing of doping metal mass, which is the same as doping single metal ion; as the doping content of Eu^{2+} is 1.0%, the diameter of catalyst grain is at its minimum value, and if the doping metal mass is increased further the diameter of catalyst grain also increases further. In short, it is an interesting problem, further research is still performed in hand[11].

Fig.1 shows the XRD pattern of samples 20, 21, 22, and 1 in series 4 and 1.

We can make out from Fig.1 that diffraction peak of doping metal ion nanometer TiO_2 widens obviously in XRD pattern, but the furthest diffraction peak (101) of pure nanometer TiO_2 was sharper in XRD pattern; which is explained that doping can reduce the diameter of TiO_2 grain. Because no typical diffraction peak of Gd^{3+} and Eu^{2+} appears in XRD pattern, we can deduce that doped Gd^{3+} and Eu^{2+} exists as little cluster.

Typical TEM images of codoped and undoped TiO_2 samples are shown in Fig.2. In comparison with the pure

Table 1 Molar ratios of Gd^{3+}/Eu^{2+} doped and degrading rate of methyl orange

Sample No.	$Eu^{2+}:Gd^{3+}$	Degrading rate/%	Sample No.	$Eu^{2+}:Gd^{3+}$	Degrading rate/%	Sample No.	$Eu^{2+}:Gd^{3+}$	Degrading rate/%
Series 1			Series 3			Series 5		
1	0:0	6	13	0.5:0	20	25	1.5:0	15
2	0:0.1	32	14	0.5:0.1	65	26	1.5:0.1	87
3	0:0.5	40	15	0.5:0.5	90	27	1.5:0.5	72
4	0:1.0	25	16	0.5:1.0	83	28	1.5:1.0	78
5	0:1.5	10	17	0.5:1.5	81	29	1.5:1.5	55
6	0:2.0	3	18	0.5:2.0	75	30	1.5:2.0	50
Series 2			Series 4			Series 6		
7	0.1:0	11	19	1.0:0	25	31	2.0:0	10
8	0.1:0.1	70	20	1.0:0.1	90	32	2.0:0.1	60
9	0.1:0.5	80	21	1.0:0.5	98	33	2.0:0.5	48
10	0.1:1.0	72	22	1.0:1.0	95	34	2.0:1.0	55
11	0.1:1.5	60	23	1.0:1.5	86	35	2.0:1.5	44
12	0.1:2.0	45	24	1.0:2.0	82	36	2.0:2.0	35

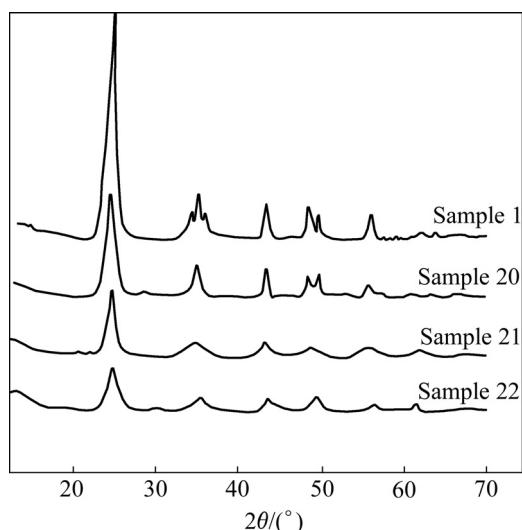


Fig.1 XRD patterns of pure TiO_2 sample and $\text{Eu}^{2+}/\text{Gd}^{3+}$ codoped TiO_2 samples

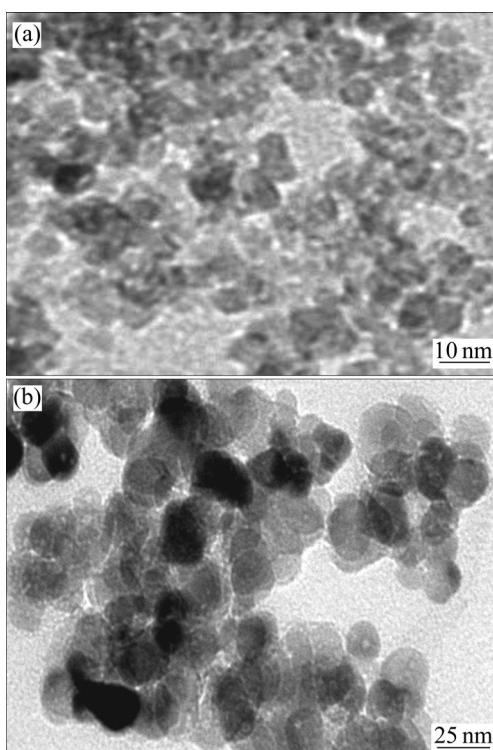


Fig.2 TEM image of codoped Gd^{3+} and Eu^{2+} TiO_2 sample (a) and pure TiO_2 sample (b)

TiO_2 sample (No.1), the codoped samples (No.20, 21 and 22) have relatively small particle size, and well dispersivity, indicating that the codoping can improve the particle morphology, and retarded the grain growth of TiO_2 during heat-treating.

3.2 UV-Vis analysis

Fig.3 shows UV-Vis diffused reflection spectra of doped samples 19, 20, 21, 22 and 23 in series 4 and pure TiO_2 sample 1. The spectra of sample 20 and sample 23

coincide together basically, spectrum of sample 21 is obvious red shift, sample 22 has good absorbance, these Gd^{3+} and Eu^{2+} four codoped samples have clearly red shift in UV-Vis spectrum and have better absorbing than only doping Eu^{2+} (sample 19) and pure TiO_2 (sample 1). So codoping Gd^{3+} and Eu^{2+} nanometer TiO_2 are favorable to absorb natural light and can increase photocatalysis activity[12]. Almost all doping of different molar ratios of $\text{Gd}^{3+}/\text{Eu}^{2+}$ can increase absorbance, but the optimum condition is $\text{Gd}^{3+}/\text{Eu}^{2+}$ equal to 0.5:1.0. The extinction capability has good coincidence relationship with photocatalysis activity, it is said that more strong extinction capability has more high photocatalysis activity.

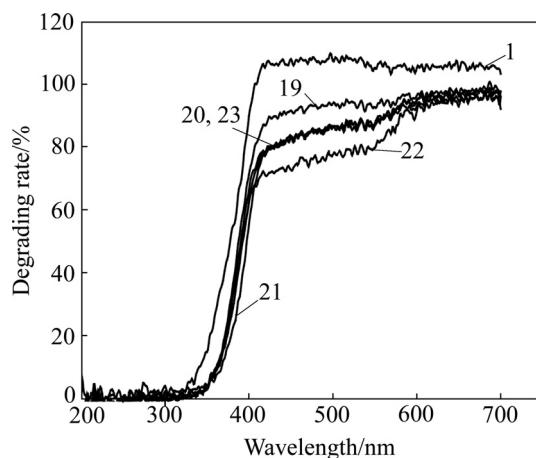


Fig.3 UV-Vis diffused reflection spectra of codoping Gd^{3+} and Eu^{2+} samples (No.20–23), doping Eu^{3+} sample (No.19) and pure TiO_2 sample (No.1)

3.3 Photocatalysis activity of doping both Gd^{3+} and Eu^{2+} samples under natural light

According to Table 1, all samples were used in photocatalysis experiment, the experiment results are shown in Fig.4 after carried out photocatalytic reaction for 5 h under natural light.

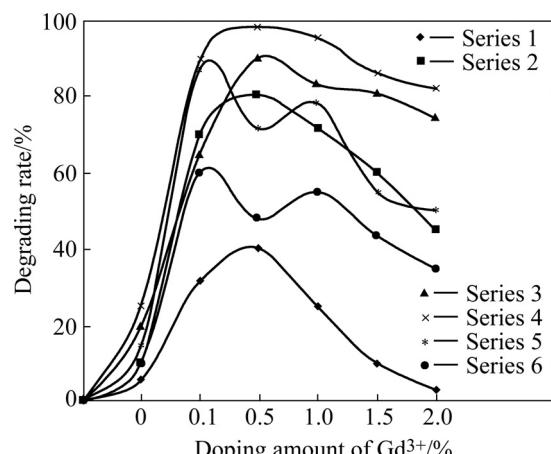


Fig.4 Photocatalysis activity comparison of codoping Gd^{3+} and Eu^{2+} samples with Eu^{2+} content being fixed

As shown in Fig.4 and Table 1, the codoped Gd³⁺ and Eu²⁺ nanometer TiO₂ can increase photocatalysis activity at a certainty proportional ratio of Eu/Gd; as the Eu²⁺ content being fixed, the photocatalysis activity increases as the Gd³⁺ content increases within limits, but if Gd³⁺ content increases continually, the photocatalysis activity will decrease. It is found that in sample 21 of series 4 the highest degrading rate of methyl orange is 98% in the case of the codoping content of Eu²⁺ and Gd³⁺ at 1.0% and 0.5%, and followed by 95% for sample 22 and 90% for sample 20. So the suitable doping content for Eu²⁺ is 0.5%–1.0% and for Gd³⁺ is 0.1%–1.0%; the optimum doping content for Eu²⁺ is 1.0% and for Gd³⁺ is 0.5%.

The experiment results also show that codoping Gd³⁺ and Eu²⁺ nanometer TiO₂ has higher photocatalysis activity than that of doping only single metal ion and pure nanometer TiO₂, it is possible to carry out photocatalysis reaction under natural light for codoping Gd³⁺ and Eu²⁺ nanometer TiO₂; simultaneously codoping Gd³⁺ and Eu²⁺ can broaden the absorbing wave range of TiO₂, and the absorption band of TiO₂ appeared red shift obviously as shown in UV-Vis diffused reflection spectrum (Fig.3), suggesting that less energy is needed and more long wave is produced in electron exciting process. because the width of absorption band is widened and the quantity of absorbing electrons is increased at given time under the same light source, therefore, the catalyzing efficiency is increased too.

We can explain photocatalysis essentiality of Gd³⁺ and Eu²⁺ codoped nanometer TiO₂ from the theory of semiconductor defect, energy band structure and carrier transfer process[13–14]. The energy level structure is changed as doping metal ions to TiO₂, the doping metal ion's energy level not only can accept excitation electron in TiO₂ excitation band, but also can absorb photon and let its electron jump to conduction band of TiO₂; because the doping metal ion's energy level locates at forbidden band, the long wave photons can be absorbed and the width of absorbance wave for TiO₂ is broadened, the solar energy can be utilized effectively. At the same time, the photoproduction electron (e⁻) in conduction band and photoproduction positive hole (h⁺) in excitation band of TiO₂ can be captured by the doping metal ion's energy level, and let them separate each other. So the recombination possibility of electron and positive hole is decreased, and the carrier lifespan is prolonged, the quantity of photoproduction electron and positive hole is increased at given time and given cubage; the chance of redox which transferred by carrier at interface is increased, the photocatalysis efficiency of TiO₂ is increased too.

Gd³⁺ and Eu²⁺ have an equal electron configuration, and their energy level structure are similar too; the minimum excitation energy state of Gd³⁺ is $^6P_{7/2}$, its wavelength is at about 32113 cm⁻¹; Gd³⁺ can match well with Eu²⁺energy band at 4f⁶5d. According to Dexter energy transfer theory, Gd³⁺ can transfer energy to Eu²⁺. Owing to superposition is existed in excitation spectrum of Gd³⁺ and Eu²⁺[15], the incident light can be absorbed at the same time by Gd³⁺ and Eu²⁺, the competitive absorbing is occurred between Gd³⁺ and Eu²⁺; there are positive and negative inflection to widen TiO₂ absorption spectrum. The process of Gd³⁺ transfers energy to Eu²⁺ can broaden TiO₂ absorption spectrum, the competitive absorbing can reduce TiO₂ absorption spectrum; so there is an optimum doping molar ratio of Gd³⁺/Eu²⁺, just like as that shown in Fig.4.

4 Conclusions

1) Codoping Gd³⁺ and Eu²⁺ nanometer TiO₂ can increase the photocatalysis activity at a certainty proportional ratio of Eu²⁺/Gd³⁺; the suitable doping content for Eu²⁺ is 0.5%–1.0% and for Gd³⁺ 0.1%–1.0%; the optimum doping content for Eu²⁺ is 1.0% and for Gd³⁺ 0.5%.

2) The process of Gd³⁺ transfers energy to Eu²⁺ is the primary reason for the increase of extinction capability and widening of absorb wave range for codoping Gd³⁺ and Eu²⁺ nanometer TiO₂.

3) Pure TiO₂ only absorbs at $\lambda=253.7$ nm, while the codoping Gd³⁺ and Eu²⁺ nanometer TiO₂ extends greatly the absorb wave range, it increases extinction capability and utilization ratio of natural light. Therefore it is possible to use natural light directly as reaction light source.

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(Edited by LAI Hai-hui)