

学校编码：10384

分类号\_\_\_\_\_密级\_\_\_\_\_

学号：20520130153813

UDC\_\_\_\_\_

廈門大學

博 士 学 位 论 文

稀土掺杂钛氧簇合物的合成、结构  
及性质研究

Syntheses, Structures and Properties of Lanthanide-Doped  
Titanium Oxo-Clusters

卢冬飞

指导教师姓名： 龙腊生教授

林文斌教授

专业名称： 无机化学

论文提交日期： 2016年06月

论文答辩日期： 2016年月

学位授予日期： 2016年月

答辩委员会主席：

评阅人：

2016年6月

稀土掺杂钛氧簇合物的合成、结构及性质研究  
卢冬飞  
指导教师  
龙腊生  
林文斌教授  
厦门大学

厦门大学博硕士学位论文摘要库



# **Syntheses, Structures and Properties of Lanthanide-Doped Titanium Oxo-Clusters**

A Dissertation Submitted to the Graduate School in Partial Fulfillment of  
the Requirements for the Degree of Doctor of Philosophy

By

Dong-Fei Lu

Supervised by

Prof. La-ShengLong & Prof. Wen-BinLin

Department of Chemistry

Xiamen University

June, 2016

厦门大学博硕士学位论文摘要库

## 厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为( )课题(组)的研究成果,获得( )课题(组)经费或实验室的资助,在( )实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学博硕士学位论文摘要库

# 厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

1. 经厦门大学保密委员会审查核定的保密学位论文，  
于 年 月 日解密，解密后适用上述授权。

2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

厦门大学博硕士学位论文摘要库



## 目录

摘要.....	I
Abstract.....	III
第一章绪论 .....	1
1.1 引言 .....	1
1.2 纯钛氧簇合物 .....	1
1.3 过渡金属掺杂钛氧簇合物 .....	11
1.4 稀土金属掺杂钛氧簇合物 .....	15
1.5 钛氧簇合物的性质研究 .....	22
1.6 本论文的选题背景与研究内容 .....	26
参考文献 .....	28
第二章基于稀土掺杂钛氧簇合物 $\text{Ln}_x\text{Ti}_y$ ( $\text{Ln} = \text{Sm}$ 和 $\text{Eu}$ ; $x = 2, 5, 8$ ; $y = 4, 10$ )的合成、结构及发光性质研究.....	39
2.1 实验部分 .....	40
2.2 实验结果与讨论 .....	45
2.3 小结 .....	53
参考文献 .....	55
第三章基于稀土掺杂钛氧簇合物 $\text{Ln}_8\text{Ti}_{10}$ ( $\text{Ln} = \text{Eu}, \text{Gd}$ 和 $\text{Sm}$ )的合 成、结构及水氧化性质研究 .....	59
3.1 实验部分 .....	60
3.2 实验结果与讨论 .....	65
3.3 小结 .....	73
参考文献 .....	74
第四章基于稀土掺杂钛氧簇合物 $\text{Ce}_6\text{Ti}_6$ 的合成、结构及光催化分解	

水性质研究 .....	79
4.1 实验部分 .....	79
4.2 实验结果与讨论 .....	82
4.3 小结 .....	87
参考文献 .....	88
<b>第五章基于稀土掺杂钛氧簇合物 <math>\text{La}_3\text{Ti}_5</math> 的合成、结构及光诱导电子转移性质研究 .....</b>	<b>90</b>
5.1 实验部分 .....	91
5.2 实验结果与讨论 .....	93
5.3 小结 .....	98
参考文献 .....	102
<b>第六章总结与展望 .....</b>	<b>105</b>
6.1 总结 .....	105
6.2 展望 .....	106
<b>附录 1 簇合物的部分键长(<math>\text{\AA}</math>)和键角(<math>^\circ</math>) .....</b>	<b>107</b>
<b>附录 2 在学期间发表的论文 .....</b>	<b>135</b>
<b>致谢 .....</b>	<b>136</b>

---

<b>Abstract in Chinese.....</b>	<b>I</b>
<b>Abstract in English .....</b>	<b>III</b>
<b>Chapter 1 Introduction.....</b>	<b>1</b>
1.1 Preface .....	1
1.2 Titanium Oxo-Clusters.....	1
1.3 Transition metal doped Titanium Oxo-Clusters.....	11
1.4 Lanthanide-doped Titanium Oxo-Clusters .....	15
1.5 Properties of Titanium Oxo-Clusters .....	22
1.6 The background and research contents.....	26
Reference .....	28
<b>Chapter 2 Syntheses, Structures and Photoluminescence Properties of Lanthanide-doped Titanium Oxo-Clusters based on <math>\text{Ln}_x\text{Ti}_y</math> (<math>\text{Ln} =</math> <math>\text{Sm}</math> and <math>\text{Eu}</math>; <math>x = 2, 5, 8</math>; <math>y = 4, 10</math>). .....</b>	<b>39</b>
2.1 Experimentation .....	40
2.2 Results and Discussions.....	45
2.3 Conclusion.....	53
Reference .....	55
<b>Chapter 3 Syntheses, Structures and Water Oxidation Properties of Lanthanide-doped Titanium Oxo-Clusters based on <math>\text{Ln}_8\text{Ti}_{10}</math> (<math>\text{Ln} = \text{Eu}</math>, <math>\text{Sm}</math> and <math>\text{Gd}</math>). .....</b>	<b>59</b>
3.1 Experimentation .....	60
3.2 Results and discussion.....	65
3.3 Conclusion.....	73
References .....	74

<b>Chapter 4 Syntheses, Structures and Photocatalysis water splitting Properties of Lanthanide-doped Titanium Oxo-Clusters based on Ce<sub>6</sub>Ti<sub>6</sub>.....</b>	<b>79</b>
4.1 Experimentation .....	79
4.2 Results and Discussions.....	82
4.3 conclusion .....	87
Reference .....	88
<b>Chapter 5 Syntheses, Structures and Light-induced Electron Transfer Properties of Lanthanide-doped Titanium Oxo-Clusters based on La<sub>3</sub>Ti<sub>5</sub>.....</b>	<b>90</b>
5.1 Experimental section .....	91
5.2 Results and discussions .....	93
5.3 Conclusions .....	98
References .....	102
<b>Chapter 6 Summary and Outlook.....</b>	<b>105</b>
6.1 Summary .....	105
6.2 Outlook.....	106
<b>Appendix I Selected bond lengths (Å)and angles ( °) of compounds in the thesis.....</b>	<b>107</b>
<b>Appendix II Published papers during the study period.....</b>	<b>135</b>
<b>Acknowledgement.....</b>	<b>136</b>

## 摘要

光解水制氢被认为是解决能源危机的最佳途径之一。众所周知,  $\text{TiO}_2$  具有良好的光催化性质, 在早期为了便于大家更好的理解其结构与化学活性的关系, 而引入钛氧簇[Titanium oxo-clusters (TOCs)]作为它的模型。但是由于钛氧簇的禁带宽度值接近或者大于锐钛矿型  $\text{TiO}_2$  的禁带宽度值, 于是人们考虑将其它金属离子引入到钛氧簇中以减小其禁带宽度值。最近的研究表明, 掺杂稀土的  $\text{TiO}_2$  其催化活性及在催化过程中的稳定性均得以增强。据我们所知, 目前有关稀土掺杂钛氧簇合物的文献非常少, 而主要研究的是晶体结构, 只有一篇对其性质进行了报道, 且文献中报道的该类簇合物中稀土金属掺杂数目最大为二。基于以上背景, 我们探索了稀土掺杂钛氧簇合物的合成条件, 合成了一系列稀土掺杂钛氧簇合物, 并解析了它们的晶体结构及详细研究了其的光学性质、光电化学性质以及光催化性质。具体内容如下:

一、以对叔丁基苯甲酸为配体, 通过溶剂热法合成了具有高稳定性稀土掺杂钛氧金属簇合物  $\text{Ln}_2\text{Ti}_4$  ( $\text{Ln} = \text{Eu}$  (1),  $\text{Gd}$  (2)和 $\text{Sm}$  (3));  $\text{Ln}_5\text{Ti}_4$  ( $\text{Ln} = \text{Ce}$  (4),  $\text{Eu}$  (5),  $\text{Sm}$  (6),  $\text{Pr}$  (7)和 $\text{Nd}$  (8));  $\text{Ln}_8\text{Ti}_{10}$  ( $\text{Ln} = \text{Eu}$  (9)和 $\text{Sm}$  (10))三个系列。研究了簇合物1, 5, 9在甲苯中的荧光激发光谱和发射光谱, 测试了三种簇合物1, 5, 9在甲苯中的量子效率分别为7.05 %、29.63 %、45.33 %和荧光寿命分别为 $1.08923 \pm 0.01313$  ms、 $1.10652 \pm 0.01049$  ms、 $1.26905 \pm 0.00746$  ms。

二、以对叔丁基苯甲酸为配体, 通过溶剂热法合成了五个同构异质稀土掺杂钛氧簇合物 $[\text{Ln}_8\text{Ti}_{10}(\mu_3\text{-O})_{14}(\text{tbba})_{34}(\text{Ac})_2(\text{H}_2\text{O})_4(\text{THF})_2] \cdot 2\text{Htbba}$  ( $\text{Ln} = \text{Eu}$  (9),  $\text{Sm}$  (10),  $\text{Gd}$  (11),  $\text{Nd}$  (12),  $\text{Tb}$  (13);  $\text{Htbba} = 4\text{-tert-butylbenzoic acid}$ ,  $\text{Ac}^- = \text{acetate}$ )。该系列簇合物是目前报道的掺杂稀土量最大的稀土掺杂钛氧簇合物。光催化水氧化性质研究表明, 该系列簇合物具有较好的化学稳定性和高效的水氧化性能。簇合物9-11水氧化法拉第效率分别为77.3 %、53.7 %、46.5 %; TONs 分别为2920、631、633; TOFs 分别  $973 \text{ h}^{-1}$ 、 $210 \text{ h}^{-1}$ 、 $211 \text{ h}^{-1}$ 。其水氧化性能差距较大可能是由于它们的禁带宽度不同引起的。

三、以特戊酸为配体, 合成出十二核稀土掺杂钛氧簇合物:  $\text{Ce}_6\text{Ti}_6(\text{OH})_8\text{O}_6(\text{CH}_3\text{COO})_4((\text{CH}_3)_3\text{CCOO})_{18}(\text{THF})_3(\text{H}_2\text{O})_6$  (14), 紫外漫反射实验表

明与商用 P25 相比, 该簇合物的吸收光谱发生了红移。对比相同条件下光催化水分解实验, 簇合物 **14** 的光催化分解水性能比商用 P25 有显著提高。

四、以对叔丁基苯甲酸为配体, 通过溶剂热技术合成了一个高稳定性的稀土掺杂钛氧簇合物:  $\text{La}_3\text{Ti}_5(\mu_3\text{-O})_6(\text{C}_5\text{H}_8\text{O}_2)_2(\text{C}_{11}\text{H}_{13}\text{COO})_{15}(\text{THF})$  (**15**), 探讨了该簇合物在模拟太阳光下作为催化剂是否具有实现电子转移产氢的性质。

**关键词:** 钛氧簇合物 稀土掺杂钛氧簇 荧光 水氧化 光催化

## Abstract

Photoinduced water splitting is regarded as one of the most promising energy sources for the preparation of hydrogen. Titanium oxo-clusters (TOCs), as the earliest known model water oxidation catalysts (WOCs) of  $\text{TiO}_2$ , offer an opportunity to understand the relationship between structure and chemical reactivity. Because the band gap of the TOCs is often close to or even larger than that of anatase, various metal ions are introduced into the TOCs to reduce their band gaps. Recent studies have demonstrated that, in addition to enhancing the photocatalytic activity, lanthanide-doped  $\text{TiO}_2$  can also increase the stability of the most photoactive anatase phase. However, lanthanide-doped TOCs remain rare. To the best of our knowledge, only ten lanthanide-doped TOCs have been reported, and the largest number of lanthanide ions doped in TOCs is 2. Furthermore, only one literature was investigated on the property of the lanthanide-doped TOCs. Based on the above background, we reported in this dissertation the syntheses, crystal structures, fluorescent, photoelectric chemical and photocatalytic properties of the lanthanide-doped TOCs. The specific contents are as follows:

1. A series of lanthanide-doped TOCs,  $\text{Ln}_2\text{Ti}_4$  ( $\text{Ln} = \text{Eu}$  (**1**),  $\text{Gd}$  (**2**), and  $\text{Sm}$  (**3**));  $\text{Ln}_5\text{Ti}_4$  ( $\text{Ln} = \text{Ce}$  (**4**),  $\text{Eu}$  (**5**),  $\text{Sm}$  (**6**),  $\text{Pr}$  (**7**) and  $\text{Nd}$  (**8**));  $\text{Ln}_8\text{Ti}_{10}$  ( $\text{Ln} = \text{Eu}$  (**9**) and  $\text{Sm}$  (**10**)), were synthesized through the solvothermal reaction of rare-earth salts,  $\text{Ti}(\text{O}^i\text{Pr})_4$  and 4-*tert*-butylbenzoic acid ligand. The phosphorescent life times of the clusters were  $1.08923 \pm 0.01313$  ms for **1**,  $10652 \pm 0.01049$  ms for **5** and  $1.26905 \pm 0.00746$  ms for **9**. The quantum yields (QY) in toluene were 7.050 %, 29.63 % and 45.33 % for **1**, **5** and **9**, respectively.

2. Five lanthanide-doped TOCs,  $[\text{Ln}_8\text{Ti}_{10}(\mu_3\text{-O})_{14}(\text{tbba})_{34}(\text{Ac})_2(\text{H}_2\text{O})_4 \cdot (\text{THF})_2] \cdot 2\text{Htbba}$  ( $\text{Ln} = \text{Eu}$  (**9**),  $\text{Sm}$  (**10**),  $\text{Gd}$  (**11**),  $\text{Nd}$  (**12**),  $\text{Tb}$  (**13**);  $\text{Htbba} = 4$ -*tert*-butylbenzoic acid,  $\text{Ac}^- = \text{acetate}$ ), were synthesized through a solvothermal reaction of  $\text{Ln}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$  and 4-*tert*-butylbenzoic acid ligand. Investigation on photocatalytic activity of **9-11** revealed that these stable compounds are efficient

catalysts for photoinduced water oxidation. The Faraday efficiencies are 77.3 % for **9**, 53.7 % for **10**, and 46.5 % for **11**, the turnover numbers (TONs) are 2920 for **9**, 631 for **10**, and 633 for **11**, and the turnover frequencies (TOFs) are 973 h<sup>-1</sup> for **9**, 210 h<sup>-1</sup> for **10**, and 211 h<sup>-1</sup> for **11**. The differences in the photocatalytic activity among these compounds are related to the differences in their band gaps.

3. A lanthanide-doped TOC, Ce<sub>6</sub>Ti<sub>6</sub>(OH)<sub>8</sub>O<sub>6</sub>(CH<sub>3</sub>COO)<sub>4</sub>((CH<sub>3</sub>)<sub>3</sub>CCOO)<sub>18</sub>(THF)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub> (**14**), was synthesized through a solvothermal reaction of cerium(III) sulfate octahydrate and Pivalic acid ligand. UV/vis spectroscopy of the cluster reveals that the optical band gap is red-shifted with respect to anatase phase reported. Investigation on the photocatalytic property of cluster **14** revealed that its photocatalytic effect is significantly better than that of P25.

4. A new lanthanide-doped TOC, La<sub>3</sub>Ti<sub>5</sub>(μ<sub>3</sub>-O)<sub>6</sub>(C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>11</sub>H<sub>13</sub>COO)<sub>15</sub>(THF)] (**15**), was synthesized through a solvothermal reaction of lanthanum acetylacetonate and with 4-*tert*-butylbenzoic acid ligand. The light induced electron transfer in the cluster **15** under the simulated solar spectrum was discussed.

**Keywords:** Titanium oxo-clusters (TOCs); lanthanide-doped TOCs; luminescence; water oxidation catalysts (WOCs); photocatalytic



Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to [etd@xmu.edu.cn](mailto:etd@xmu.edu.cn) for delivery details.

厦门大学博硕士论文摘要库