学校编码：10384　　分类号__密级__
学　　号：20720100153473　　UDC___

厦门大学

博 士 学 位 论 文

基于微混合技术的可见光响应 TiO_2 光阳极的制备及其光电化学性能研究

Micromixing-assisted Fabrication and Photo-electrochemical Performance Investigation of TiO_2 Photoanodes with Visible Light Response

许 超

指导教师姓名：　冯 祖 德 教 授
专 业 名 称：　材　　料　　学
论文提交日期：　2015 年 1 月
论文答辩日期：　2015 年 1 月
学位授予日期：　2015 年　　月

答辩委员会主席：_____
评　　阅　　人：_____

2015 年 1 月

Micromixing-assisted Fabrication and Photo-electrochemical Performance Investigation of TiO_2 Photoanodes with Visible Light Response

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

By

Chao Xu

Directed by **Prof. Zude Feng**

Department of Materials Science and Engineering, College of Materials, Xiamen University

January, 2015

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

摘要

基于 TiO_2 半导体特殊的光电化学性能，其有望成为绿色、环保的新型金属防腐技术中最为重要的光阳极材料。但是，TiO_2 存在可见光利用率低、光量子效率不高等限制其实际应用的问题。此外，由于传统混合方式在快速沉淀体系中难以有效调控均相化学过程，导致碱性液相环境制备有序 TiO_2 薄膜至今仍无法实现。基于上述考虑，本论文提出使用微混合设备辅助在碱性液相环境下制备出形貌可控的 TiO_2 薄膜光阳极，并通过沉淀剂对产物进行选择性原位掺杂改性。通过数值模拟及实验测试深入研究了制备条件和掺杂对 TiO_2 薄膜光阳极光电化学性能的影响。本论文的主要研究内容和结果如下：

1、基于自行设计并制造的多孔分散微结构混合器，对液−液快速沉淀体系进行数值模拟及实验研究。结果表明，微混合器可在极短的时间内完成对液−液反应物的高效混合并有效抑制反应混合液中的均相化学反应，反应物流量、分散介质尺寸等对一次粒子的平均粒径及粒度分布有显著影响。

2、以微混合技术为背景，设计出一种在低温、碱性环境中高效合成有序锐钛矿纳米 TiO_2 薄膜的新工艺。实验发现，通过调节微观混合及液相沉积参数，产物的表面形貌可得到有效调控。当微观混合质量流率、沉积时间、温度分别为 0.60 m/s、50 min、80 ℃ 时，制得的 TiO_2 薄膜质量最佳。

3、通过调整 N 源浓度，制备出不同 N 掺杂物含量的 TiO_2 薄膜光阳极。结果表明，N 已进入 TiO_2 晶格并拓展了 TiO_2 的可见光响应区间，$CO(NH_2)_2$ 浓度对薄膜生长效率和 N 掺杂能力有显著影响。N-TiO_2 光阳极具有优良的可见光诱导光电化学活性，在可见光照射下能对金属起到有效的光生阴极保护作用。

4、使用 $Al(NO_3)_3$ 和 $FeCl_3$ 分别作为 Al 源和 Fe 源，制备出 N/Al、N/Fe 共掺杂 TiO_2 薄膜光阳极。Al^{3+}、Fe^{3+}进入 TiO_2 晶格并取代 Ti^{4+}的位置，N/Al、N/Fe 共掺杂协同作用抑制了薄膜晶粒长大，提高了 TiO_2 光阳极的可见光响应活性和光量子效率，并抑制光生电子与价带中光生空穴的复合。

关键词：微混合技术；TiO_2 光阳极；掺杂改性；可见光响应；光电化学性能

Abstract

TiO_2 semiconductor is expected as the most important photoanode material applied for the novel green and environmental friendly metal anticorrosion technology, because of its unique photoelectrochemical properties. Nevertheless, the inherent disadvantages of the TiO_2, lies in their limited visible light utilization and quantum yield, have extremely restricted their practical applications. Moreover, the synthesis of well-ordered TiO_2 thin films from alkaline solution is still challenging due to the fact that the traditional mixing process possesses several disadvantages in controllable homogenous chemistry. Therefore, the work described in this paper is devoted to the preparation of TiO_2 thin film photoanodes from alkaline solutions with controllable morphology. In addition, several reactants are employed to doping anions and cations into the TiO_2 product. The effects of the operation conditions and doping modifications on the photoelectrochemical performance of the TiO_2 thin film photoanodes are investigated based on the numerical simulation and experimental measurements. The main research contents and results of this work were summarized as follows:

1. Based on the use of home-built micromixer, the liquid-liquid reaction system with fast precipitation process is investigated through numerical simulation and experimental measurements. It is found that the micromixer is advantageous for the ultrafast mixing at the microscale, and the homogeneous chemistry in the reactant solutions can be efficiently inhibited. The initial inlet velocity of the reactant solutions and the diameter of the microfiltration membrane have major impacts on the average size and distribution of the primary nano particles.

2. A novel micromixing-assisted route is designed to efficiently synthesize well-ordered anatase-TiO_2 thin films from alkaline solutions at low temperatures. The experimental results indicate that the surface morphology of the product can be controlled by carefully operating the parameters of micromixing and liquid phase deposition process. The quality of the of the surface morphology can be significantly

increased when the microxming mass flow rate, deposition time and preparation temperature is 0.60 m/s, 50 min and 80 ℃, respectively.

3. The TiO_2 thin films photoanodes with various N contents are successfully synthesized through adjusting the concentration of the N-containing compounds. It is found that the N is well incorporated into the TiO_2 lattice and thus shifting the absorption zone of the TiO_2 to the visible domain. Intriguingly, we find that the concentration of $CO(NH_2)_2$ plays a significant role in affecting the films growth rate and the N-doping capability. The as-prepared N-TiO_2 photoanodes exhibit excellent visible light-induced photoelectrochemical activities and can provide an effective photogenerated cathodic protection for the coupled metal electrode.

4. The TiO_2 thin films photoanodes co-doped with N/Al and N/Fe are successfully synthesized by using $Al(NO_3)_3$ and $FeCl_3$ as Al and Fe source, respectively. The results indicate that the Ti^{4+} in TiO_2 lattice is substituted by Al^{3+} and Fe^{3+} ions. The synergistic effect of N/Al and N/Fe co-doped has the benefit to restrain grain growth, as well as improving the visible light response activity of the TiO_2 photoanodes. Moreover, the recombination rate of photogenerated electron-hole is efficiently restricted due to the impregnation of Al and Fe.

Keywords: Micromixing technology; TiO_2 photoanodes; Doping modification; Visible light response; Photolectrochemical performance

目 录

Table of Contents