View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Xiamen University Institutional Repository

学校编码：10384　　分类号_____密级_____
学　　号：20520081151653　　UDC_____

厦门大学

硕　士　学　位　论　文

基于纳米半导体的光催化还原体系的研究及其在元素测定和形态分析的应用

Nanosemiconductor-based photocatalytic reduction systems for element determination and speciation analysis

李华敏

指 导 教 师：王 秋 泉 教 授
专 业 名 称：分 析 化 学
论文提交日期：2011 年　　月
论文答辩时间：2011 年　　月
学位授予日期：2011 年　　月

答辩委员会主席：_____
评　　阅　　人：_____

2011 年　月

厦门大学博硕士论文摘要库

基于纳米半导体的光催化还原体系的研究及其在元素测定及形态分析的应用　李华敏　指导教师　王秋泉 教授　厦门大学

Nanosemiconductor-based photocatalytic reduction systems for element determination and speciation analysis

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

By

Huamin Li

Supervised by

Prof. Qiu-Quan Wang

Department of Chemistry

Xiamen University

December, 2011

厦门大学博硕士论文摘要库

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

厦门大学博硕士论文摘要库

目录

摘要.....I

Abstract.....IV

第一章 前言 1

1.1 化学蒸气发生进样技术.....1

1.1.1 蒸气发生进样技术.....1

1.1.2 蒸气发生进样的主要优点.....1

1.1.3 氢化物/冷原子蒸气发生法.....2

1.1.4 光致蒸气发生法(photo-CVG).....5

1.1.5 卤化物蒸气发生法.....13

1.1.6 羰基衍生物发生法.....15

1.1.7 烷基衍生物发生法.....15

1.1.8 氧化物发生法.....17

1.1.9 螯合物蒸气发生法.....18

1.2 纳米半导体光催化.....18

1.2.1 非匀相光催化反应.....18

1.2.2 二氧化钛光催化.....20

1.2.3 二氧化锆光催化.....22

1.3 元素形态分析 23

1.3.1 形态分析.....23

1.3.2 联用技术在形态分析领域中的应用.....24

1.4 本工作的设想及工作内容.....25

1.5 参考文献.....26

第二章UV/Ag-TiO_2光催化还原装置用于碲的离子交换色谱-原子荧光光谱形态分析 40

2.1 前言.....40

厦门大学博硕士论文摘要库

2.2 实验部分 41
2.2.1 试剂 41
2.2.2 仪器 42
2.2.3 分析步骤 44
2.3 结果与讨论 44
2.3.1 色谱分离条件的优化 44
2.3.2 接口条件优化 46
2.3.3 方法评价 52
2.3.4 HPLC-UV/Ag-TiO_2 -HG-AFS应用于实际样品的分析测定 52
2.4 结论 53
2.5 参考文献 53
第三章 基于半导体光催化的蒸气发生进样新技术的硒的测定及其形态分析 55
3.1 前言 55
3.2 实验部分 57
3.2.1 试剂 57
3.2.2 仪器 57
3.2.3 分析步骤 58
3.2.4 溶胶-凝胶法制备纳米TiO_2、ZrO_2薄膜和贵金属沉积TiO_2、ZrO_2薄膜 59
3.2.5 光催化蒸气发生效率 61
3.3 结果与讨论 61
3.3.1 基于TiO_2的光催化还原体系 61
3.3.2 基于ZrO_2的光催化还原体系 67
3.3.3 产物确认与机理探讨 67
3.3.4 方法评价 69
3.3.5 实际样品分析 70
3.4 结论 71
3.5 参考文献 73

厦门大学博硕士论文摘要库

第四章 基于纳米ZrO_2光催化还原的冷蒸气发生进样技术在汞形态分析中的应用 76

4.1 前言 76

4.2 实验部分 77

4.2.1 试剂 77

4.2.2 仪器 77

4.2.3 分析步骤 78

4.3 结果与讨论 79

4.3.1 色谱条件的优化 79

4.3.2 甲酸浓度的优化 80

4.3.3 pH 的影响 80

4.3.4 甲酸流速优化 81

4.3.5 氩气流速的影响 82

4.3.6 方法的评价 83

4.3.7 HPLC- UV/ZrO_2-AFS汞元素形态分析 84

4.3.8 不同体系比较 84

4.4 结论 85

4.5 参考文献 85

第五章 总结与展望 89

在学期间发表的论文 90

致谢 91

厦门大学博硕士论文摘要库

Table of Contents

Abstract (in Chinese) I

Abstract (in English) IV

Chapter 1 Preface 1

1.1 Chemical vapor generation technique 1

1.1.1 Vapor generation sample introduction technique 1

1.1.2 Merits of vapor generation sample introduction technique 1

1.1.3 Hydride /cold vapor generation 2

1.1.4 Photo chemical vapor generation 5

1.1.5 Halide generation 13

1.1.6 Cabonyls generation 15

1.1.7 Alkyls generation 15

1.1.8 Oxide generation 17

1.1.9 Chelate generation 18

1.2 Photocatalysis of nano semiconductor 18

1.2.1 Heterogenerous photocatalysis 18

1.2.2 Photocatalysis of TiO_2 20

1.2.3 Photocatalysis of ZrO_2 22

1.3 Elemental speciation analysis 23

1.3.1 Speciation analysis 23

1.3.2 Hyphenated techniques 24

1.4 Research proposal 25

1.5 References 26

Chapter 2 Development of UV/Ag-TiO_2 photocatlytic reaction device for the tellurium speciaton by ion-exchange chromatography coupled with atomic fluorescence spectrometry 40

厦门大学博硕士论文摘要库

2.1 Introduction 40

2.2 Experimental 41

2.2.1 Reagents 41

2.2.2 Instruments 42

2.2.3 Procedures 44

2.3 Results and discussion 44

2.3.1 Optimization of the separation conditions for Te species 44

2.3.2 Development of the interface 46

2.3.3 Analytical performance 52

2.3.4 Analytical applications 52

2.4 Conclusion 53

2.5 References 53

Chapter 3 Nanosemiconductor-based photocatalytic vapor generation systems for subsequent selenium determination and speciation 55

3.1 Introduction 55

3.2 Experimental 57

3.2.1 Reagents 57

3.2.2 Instruments 57

3.2.3 Procedures 58

3.2.4 Preparation of nano TiO_2 and ZrO_2 as well as noble metal loaded TiO_2 and ZrO_2 film by sol-gel method 59

3.2.5 Photocatalytic vapor generation efficiency 61

3.3 Results and discussion 61

3.3.1 TiO2-based photocatalytic reduction systems 61

3.3.2 ZrO2-based photocatalytic reduction systems 67

3.3.3 Generated species identification 67

3.3.4 Analytical performance 69

3.3.5 Analytical applications 70

3.4 Conclusion 71

厦门大学博硕士论文摘要库

3.5 References 73

Chapter 4 A novel UV/ZrO_2 photocatalytic reduction device for mercury speciation analysis 76

4.1 Introduction 76

4.2 Experimental 77

4.2.1 Instruments 77

4.2.2 Reagents 77

4.2.3 Analytical procedure 78

4.3 Results and discussion 79

4.3.1 Optimization of the separation conditions for Hg species 79

4.3.2 Optimization of formic acid concentration 80

4.3.3 Effect of pH 80

4.3.4 Optimization of the flow rate of formic acid 81

4.3.5 Optimization of the flow rate of argon gas 82

4.3.6 Analytical performance 83

4.3.7 Analytical applications 83

4.3.8 Comparion of different vapor generation systems 84

4.4 Conclusion 85

4.5 References 85

Chapter 5 Summary and prospect 88

Publications 90

Acknowledgement 91

厦门大学博硕士论文摘要库

摘要

尽管元素的蒸气发生技术发展到今天已经有一百多年的历史，但这项技术在现代分析科学中仍然扮演着重要的角色，并且仍在不断的创新、发展。伴随着蒸气发生新技术新方法的不断涌现，可蒸气发生元素的范围不断扩大，原子光谱分析的检测灵敏度不断提高，蒸气发生进样已经成为测量复杂基体中痕量特别是超痕量元素的一种常规的进样方法。化学蒸气发生法主要包括氢化物发生、卤化物发生、烷基化物发生、氧化物发生和光诱导/催化蒸气发生等方法。常用的蒸气发生进样方法是采用硼氢化物-酸体系的传统氢化物发生法，此方法进样效率高，但是也有以下缺欠：（1）易受过渡金属离子如Cu^{2+}、Ni^{2+}、Co^{2+}等的干扰；（2）硼氢化物溶液（$NaBH_4$或KBH_4）不稳定，必须在碱性溶液中才能保存，而且要现配现用；（3）易带来污染，硼氢化物是一个潜在的试剂污染源，较高的试剂空白影响了检测限的改善；（4）氢化反应需要一定的酸度，某些元素如锡和铅等对酸性条件要求比较苛刻；（5）价态歧视严重，对待测元素的氧化还原状态要求苛刻；（6）体系产生的大量氢气在等离子体特别是低能等离子体作为激发源的分析过程中，会造成等离子体的不稳定，反向功率的增大，甚至引起等离子体的熄灭。所以，需要改进该体系和发展高效的蒸气发生新体系以克服上述传统氢化物发生体系的不足。

近年来的研究表明，元素的存在形态决定了其在环境和生命过程中的行为。元素的形态分析的重要性越来越凸显出来。联用技术已经成为元素形态分析中最广泛应用的技术。由于高效液相色谱（HPLC）和原子荧光光谱（AFS）使用简便、选择性和灵敏度高、经济实用等优点，它们通过高效的蒸气发生在线接口链接联合使用已在可蒸气发生元素的形态分析领域广泛应用。

本论文旨在发展基于纳米半导体材料的光催化蒸气发生技术，通过对纳米TiO_2进行改性和寻找光催化还原能力更强的纳米半导体材料来发展新的光催化还原体系，提高光催化蒸气发生效率，并将其作为HPLC与AFS的接口，应用于一系列元素的形态分析。

厦门大学博硕士论文摘要库

本论文分为五个部分：

第一章主要是对蒸气发生进样技术进行了综述，归纳总结了现今被广泛采用的蒸气发生技术和联用技术在元素形态分析中的应用；介绍了纳米半导体的非均相光催化反应。

第二章研究了UV/Ag-TiO_2光催化在线预还原Te(VI)的新方法，通过在TiO_2表面沉积贵金属Ag，降低光生电子–空穴的复合几率，提高了光催化还原能力，解决了Te(VI)直接与KBH_4/NaOH-HCl反应还原效率太低、无法直接在线进样和原子化的问题。优化了Ag的沉积量，空穴捕获剂的种类、浓度和流速等条件。Te(VI)的蒸气发生效率提高到 70%。并以UV/Ag-TiO_2光催化还原装置与KBH_4/NaOH-HCl联合为接口，发展了阴离子交换液相色谱分离–在线还原–原子荧光光谱检测体系，实现了无机Te(VI)和Te(IV)的分离检测。Te(VI)和Te(IV)的检测限分别达到 2.6 和 1.6 ng mL^{-1}。该体系应用于实际水样中Te的形态分析。

第三章主要是通过在TiO_2表面沉积贵金属和利用ZrO_2（光生电子具有更强的还原能力）的强的光催化还原性质，建立了UV/Ag-TiO_2-HCOOH和UV/ZrO_2-HCOOH光催化还原新体系，作为Se的新型直接光催化蒸气发生体系，将光致蒸气发生效率提高至 70%，并鉴定了光催化还原产物、对其光催化机制进行了研究。当使用AFS作为检测器时，四种典型的Se形态（Se(IV)，Se(VI)，SeCys和SeMet）在UV/Ag-TiO_2-HCOOH体系中的 LODs (3σ) 分别为 1.2、1.8、7.4和0.9 ng mL^{-1}；在UV/ZrO_2-HCOOH体系中分别为 0.7、1.0、4.2 和0.5 ng mL^{-1}，RSD低于 5.1% (n = 9，1 μg mL^{-1})。当使用ICP-MS作为检测器时，这四种Se形态的LODs在UV/Ag-TiO_2-HCOOH体系中分别达到 10、14、18 和 8 pg mL^{-1}；在UV/ZrO_2-HCOOH 体系中分别达到 6、7、10 和 5 pg mL^{-1}，RSD低于 4.4% (n = 9，10 ng mL^{-1})。设计制作的UV/Ag-TiO_2-HCOOH和UV/ZrO_2-HCOOH光催化还原装置，进一步作为离子对HPLC与AFS联用接口，应用于富硒酵母的硒形态分析。

第四章发展了UV/ZrO_2-HCOOH光催化还原新体系作为Hg冷原子蒸气发生原子化新技术，并将其作为HPLC与AFS的联用接口，实现了无机汞，氯化甲基汞，氯化乙基汞和氯化苯基汞的分离检测。这四种汞形态的检测限分别为 20，20，10，和 40 pg mL^{-1}，RSD低于 3.9%。该方法成功地应用于海产品中Hg的形

态分析。

第五章总结了本硕士论文的研究工作，并对进一步开展的研究工作进行了展望。

关键词：化学蒸气发生 光催化还原 纳米半导体 形态分析 联用技术 碲 硒 汞

厦门大学博硕士论文摘要库

Abstract

Although the sample introduction technique of chemical vapor generation (CVG) has been developed for over 100 years, it sill plays an important role today in modern analytical atomic spectrometry. The technique has become popular for the determination of trace elements in the complex matrices, and new approaches continuously comes forth to improve its efficiency and expand the scope of its applications. CVG of vapor generable elements includes hydride/cold vapor generation, halide generation, alkyls generation and photo-induced and/or photo catalytic vapor generation. Among them, traditional KBH_4/NaOH-HCl system was most widly used. But some drawbacks should be also noted that: (1) susceptibility to interferences from common transition metals, e.g. Cu^{2+}, Ni^{2+} and Co^{2+}; (2) tetrahydraborate (THB, $NaBH_4$ or KBH_4) is very unstable, it must be prepared daily in alkaline solution; (3) THB ($NaBH_4$ or KBH_4) is a potential source of contamination; (4) the hydride generation conditions for some element are rigour; (5) difficult to convert the species of an element existing in high oxidation state or as organic complex into volatile species; (6) large amount of hydrogen generated during the decomposition of KBH_4 reduces the stability of the plasma or even extinguishes the plasma. Hence, it is great desired to amend or substitute the traditional KBH_4/NaOH-HCl system. Photo-induced or catalytic chemical vapor generation (photo-CVG) is a newly emerging CVG technique in analytical chemistry, which provides a powerful alternative owing to its higher efficiency, simplicity, versatility, and cost-effectiveness as well as environment-friendly properties.

Recent approaches indicated that the chemical forms (species) determine the toxicity and bioavailability of an element in a biological system and/or in the environment. More and more concerns have been focused on elemental speciation from the view points of environmental and biological sciences. Hyphenated techniques, which combine a continuing separation and an element-selective and/or a

厦门大学博硕士论文摘要库

structure-specific detector, play a significant role in elemental speciation analysis. Studies of this thesis focused on the development of photo-CVG systems to enhance the efficiency of photo-CVG by loading noble metal on the surface of nano TiO_2 and/or using other nano semiconductor, e.g. ZrO_2, and the application of the proposed photo-CVG syetem together with atomic fluorescence spectrometry (AFS) to the determination and speciation analysis of some elements in environmental and biological samples.

This thesis consists of 5 chapters.

In Chapter 1, published literatures were reviewed which gives a brief introduction to the history and development of CVG techniques. Various CVG techniques and its use as an interface between analytical atomic spectrometry and continuing separation techniques (gas chromatography, high performance liquid chromatography and capillary electrophoresis) were briefly introduced. Moreover, the heterogenous photocatlaysis of nano semiconductor was also briefly introduced.

In Chapter 2, UV/Ag-TiO_2 photocatalytic reduction system for the online pre-reduction of Te(VI) before the hydride generation (HG) with KBH_4/NaOH-HCl was developed. The deposition of Ag on the surface of TiO_2 enhanced the photocatalytic activity by reducing the recombination of photogenerated electrons and holes. We also optimized the deposition mass of Ag, the concentration and flow rate of the hole scavenger. An UV/Ag-TiO_2 photocatalytic reduction device was designed and fabricated for achieving online reduction of Te(VI). The generation efficiency of Te(VI) was improved up to 70%. This device was also used as an interface between HPLC and HG-AFS for the inorganic tellurium speciation analysis. The detection of limits were 2.6 and 1.6 ng mL^{-1} for Te(VI) and Te(IV), respectively. This hephenated system was applied to Te speciation in water samples.

In Chapter 3, new UV/Ag-TiO_2 and UV/ZrO_2 systems were developed for the direct vapor generation of selenium species for the determination of selenium using AFS and ICP-MS. The LODs (3σ) of the most four typical selenium species (Se(IV), Se(VI), SeCys and SeMet) were down to 1.2, 1.8, 7.4 and 0.9 ng mL^{-1} in UV/Ag-TiO_2-HCOOH, and 0.7, 1.0, 4.2 and 0.5 ng mL^{-1} in UV/ZrO_2-HCOOH, with

厦门大学博硕士论文摘要库

the RSD lower than 5.1% (n = 9 at 1 μg mL^{-1}) when using AFS. They reached 10, 14, 18 and 8 pg mL^{-1} in UV/Ag-TiO_2-HCOOH, and 6, 7, 10 and 5 pg mL^{-1} in UV/ZrO_2-HCOOH with the RSD lower than 4.4% (n = 9 at 10 ng mL^{-1}) using ICP-MS. UV/Ag-TiO_2-HCOOH and UV/ZrO_2-HCOOH photocatalytic device were also designed and fabricated and used as interfaces between HPLC and AFS for selenium speciation in the water extractable and enzymatic extractable fractions of Se-enriched yeast.

In Chapter 4, UV/ZrO_2-HCOOH photocatalytic reduction system was developed and applied as a new vapor generation system for Hg determination and speciation analysis. The detection limits for Hg^{2+}, $MeHg^+$, $EtHg^+$ and $PhHg^+$ were 20, 20, 10 and 40 pg mL^{-1}, respectively, and the RSDs (n=6, the concentrations of mercury species were 100 ng mL^{-1}) were less than 3.9%. The proposed method HPLC-(UV/ZrO_2-HCOOH)-AFS was also applied to Hg speciation of real seafood samples, showing that both $MeHg^+$ and Hg^{2+} contamination could be found in these samples.

In Chapter 5, Conclusion of this thesis and perspectives in this area.

Keywords: Chemical vapor generation; photocatalytic reduction; nano semiconductor; speciation analysis; hyphenated technique; tellurium; selenium; mercury.

厦门大学博硕士论文摘要库

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 for delivery details.

厦门大学博硕士论文摘要库