

# 配位转化法制备纳米MS(M=Cd, Zn) 原理、动力学及其光催化CO<sub>2</sub>还原性能

作者：刘引烽

专业：材料学

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桑文斌



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2004 年上海大学博士学位论文

# 配位转化法制备纳米 $MS$ ( $M=Cd, Zn$ ) 原理、动力学 及其光催化 $CO_2$ 还原性能

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Shanghai University Doctoral Dissertation (2004)

**Preparation Principle and Synthetic Kinetics  
and the Photocatalysis of the  
Nanometer-sized MS (M=Cd, Zn)  
Prepared by Coordination Transformation**

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**Major:** Materials Science  
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• Shanghai •

# 上海大学

本论文经答辩委员会全体委员审查，确认符合上海大学博士学位论文质量要求。

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## 答辩委员会对论文的评语

刘引烽的博士论文对纳米半导体 CdS 和 ZnS 的制备、结构及其光催化还原  $\text{CO}_2$  的特性进行了系统、深入的研究。该研究是相关学科的前沿命题，具有重要的学术意义和潜在的应用价值。该论文工作的主要创新点是：

1. 论文运用配位转化法成功地制得了尺寸均匀、稳定、可控性好的纳米 CdS 和 ZnS，配合红外光谱等分析手段，提出了配位转化法的机理。系统地表征和研究了纳米半导体在不同聚合物基体中的尺寸、结构和光吸收特性，证明聚合物的配位能力是影响纳米微粒结构和尺寸的重要因素。

2. 论文系统地研究了纳米 ZnS 在聚合物膜中形成的动力学过程，提出了在存在化学反应条件下的非恒源扩散模型，建立了扩散速率方程，推演了相关的动力学参数，从而提出：可以通过配位比和聚合度，对所生成的纳米硫化物微粒的尺寸进行预测和控制。

3. 采用配位转化法制备了新型的  $\text{SiO}_2/\text{PVA}/\text{MS}$  ( $\text{M}=\text{Cd}, \text{Zn}$ ) 纳米催化剂，研究了其对  $\text{CO}_2$  的光催化还原反应活性和影响因素，所得甲醇、乙醇和甲醛等主要有机产物的产率较高。提出了纳米 MS 光催化还原  $\text{CO}_2$  反应的机理，并发现添加还原剂  $\text{Na}_2\text{SO}_3$  可提高催化反应产率。提出了提高光催化  $\text{CO}_2$  还原反应效率的途径。

论文工作严肃认真，数据可信，图表规范，条理清楚，分析合理，结论正确，做出了具有创新性的结果。在攻读博士期间，

在国内外学术刊物上发表论文 10 余篇(第一作者 SCI 收录 5 篇)。

综上所述,该同志掌握了坚实的理论基础与系统深入的专业知识,具备了独立从事科研工作的能力。论文达到了博士学位论文的水平。该论文是一篇优秀论文。答辩过程中思路清晰,表达清楚,对所提问题回答正确。

### 答辩委员会表决结果

经答辩委员会讨论,投票表决,一致同意通过刘引烽同志的  
博士学位论文答辩,并建议授予其博士学位。

答辩委员会主席: **胡行方**

2004 年 8 月 31 日

## 摘 要

光合作用是自然界对二氧化碳实现光还原反应的杰作. 如何利用光催化剂对二氧化碳实现还原是目前催化研究领域的重要课题, 也是向自然学习、模拟生物过程的重要课题. 它将废弃的二氧化碳资源加以利用, 减少其对环境的污染, 减轻温室效应, 同时充分运用太阳能能源, 是实现自然生态循环、保护环境的有效途径. 纳米半导体显著的量子尺寸效应, 使其具有较强的光催化活性; 而通过调节纳米晶粒尺寸可以改变其光学响应, 从而提高太阳能利用率, 因此已成为光催化领域的研究热点. 本文以此为背景, 综合分析了该领域的研究与发展, 运用本课题组首先提出的配位转化法制备了纳米光催化剂 MS( $M=\text{Cd}, \text{Zn}$ ), 并对二氧化碳进行光催化还原反应, 系统地研究了配位转化法制备纳米 MS 的原理和动力学、纳米 MS 的结构与制备条件间的关系、以及二氧化碳光催化还原反应机理及其影响因素等.

本文选择甲壳胺、聚乙烯醇、聚氧乙烯和聚丙烯腈共聚物等极性聚合物作为配位体, 与金属离子  $M^{2+}$  ( $M=\text{Cd}, \text{Zn}$ ) 进行配位, 并引入  $\text{Na}_2\text{S}$  溶液作为硫源, 采用配位转化方法制备了不同聚合物基体保护的纳米硫化物 MS ( $M=\text{Cd}, \text{Zn}$ ). 对配位转化法原理、制备动力学、纳米微粒的结构和尺寸研究证明, 配位转化法对于制备含有过渡金属元素化合物纳米材料具有普适性. 采用间接显色方法跟踪测定了溶液中硫离子浓度的变化, 率先研究了制备过程动力学. 根据 Fick 扩散定率, 基于非恒源及存在化学反应的扩散过程, 提出了硫离子在配合物膜中的扩散模型, 建立了其动



力学方程, 并进行模拟计算, 模拟曲线与实验结果相当吻合, 由此估算出在 PVA/ $\text{Zn}^{2+}$  配合物膜中硫离子的扩散系数  $D$  为  $9.92 \times 10^{-6} \text{ cm}^2/\text{s}$ ; 配合物转化反应的速率常数  $k$  为  $16.1 \text{ mol/L} \cdot \text{s}$ , 反应活化能  $\Delta E = 61.7 \text{ KJ/mol}$ . 根据动力学研究结果, 首次提出可以由配位比对纳米硫化物微粒尺寸进行预测, 在亚浓溶液中制备纳米 ZnS 微粒时, 其晶粒尺寸与聚合物的聚合度成正比, 而与配位比成反比. 预测的结果与实际测定值相符.

运用 IR 光谱对配位转化过程进行跟踪测定, 发现在配位转化形成纳米硫化物后, 聚合物与硫化物间仍存在配位作用, 从而提出了配位转化法制备纳米硫化物的机理. 通过 XRD、TEM、UV 等分析测试手段, 对所制备的纳米微粒进行晶体结构及微粒尺寸分析. XRD 谱分析表明, 所制备的纳米硫化物均以闪锌矿为主; XRD 衍射峰明显宽化, 同时硫化物微粒的紫外光谱中带边吸收波长明显蓝移, 说明所制备的硫化物微粒处于纳米尺度, 证明了采用配位转化法制备纳米微粒具有尺寸均匀、可控、稳定等优点; 在进行微粒尺寸估算时, 采用 EMA 方法估算和 TEM 观察结果较为接近, 而采用 Scherrer 公式估算的结果明显偏低. 制备条件对纳米微粒结构与尺寸的影响研究证明, 含有强配位基团的聚合物对纳米硫化物具有良好的保护作用; 聚合物配体与金属离子间的配位比越大、转化过程中浸渍时间越短、浸渍液  $\text{Na}_2\text{S}$  浓度越低、转化反应温度越低, 其吸收边蓝移越多, 所得纳米硫化物尺寸越小; 但浸渍液浓度和浸渍时间的影响有一定的范围.

采用气相二氧化硅负载, 通过配位转化法制备了纳米光催化剂  $\text{SiO}_2/\text{PVA}/\text{MS}(\text{M}=\text{Zn}, \text{Cd})$ , 对  $\text{CO}_2$  进行了光催化还原反应研究. 气相色谱分析表明, 催化体系中有氧气产生. 纳米 ZnS 光催化的主产物为甲醇、乙醇、甲醛及少量的硝基甲烷, 所得有机产

配位转化法制备纳米 MS(M=Cd, Zn)原理、动力学及其光催化 CO<sub>2</sub> 还原性能

物总量最多可达  $10^{-4}$  mol/(0.1g 催化剂·24h)数量级; 纳米 CdS 光催化的产物则以甲醇、甲醛及少量的硝基甲烷为主, 所得有机产物总量最多为  $10^{-5}$  mol/(0.1g 催化剂·24h)数量级, 说明纳米 ZnS 的光催化还原 CO<sub>2</sub> 能力高于纳米 CdS 光催化剂. 加入 Na<sub>2</sub>SO<sub>3</sub> 还原剂的 CdS 体系, 其催化产物还包括有较多量的乙醛, 且其催化产物总量有较大程度提高, 首次证明添加还原剂有助于光催化还原 CO<sub>2</sub> 反应. 根据催化还原产物及催化反应过程中气体体积的变化规律, 推测了纳米 MS(M=Zn, Cd)光催化还原 CO<sub>2</sub> 反应的机理. 在光照条件下, 纳米半导体产生光生电子-空穴对, 并分别向 CO<sub>2</sub>(或 HCO<sub>3</sub><sup>-</sup>)和 H<sub>2</sub>O 分子转移, 从而引发一系列的氧化还原反应, 生成甲酸、甲醛和甲醇等. 经 XPS 表征证明, 与细菌光合作用过程相似, 纳米 MS(M=Zn, Cd)中 S 也参与了还原过程. 系统研究制备条件对纳米光催化剂活性的影响表明, 制备条件不同, 其结构随之改变, 其催化活性也不相同. 配位基与金属离子之比(O/Zn 比或 O/Cd 比)增大, 浸渍液 Na<sub>2</sub>S 溶液浓度降低时, 纳米催化剂的尺寸减小, 但其活性呈先增加后减小的规律, 并非随粒径减小而单调增加; 同时, S<sup>2-</sup>过量形成金属离子空位时, 由于其本身具有较强的供电子能力, 因此可以促进 CO<sub>2</sub> 的光催化还原反应. 随着催化反应的进行, 纳米硫化物的光解反应是不可避免的. 采用 CuS 修饰, 在一定程度上可以保护催化剂, 延迟其光解作用, 从而提高催化剂的光催化活性, 延长其催化作用时间. 而对 ZnS 表面用碱性条件处理以形成 ZnO 修饰时, 其保护作用不明显.

本课题为国家自然科学基金资助项目(NSFC-69871017)“半导体纳米材料与蓝色发光器件的探索”、上海市教委自然科学基金资助项目(98QN54)“纳米催化剂与纳米吸附剂的研究”的进一步扩展.

关键词 纳米晶粒, ZnS, CdS, 聚合物配位体, 配位转化法, 光催化还原, CO<sub>2</sub>

## Abstract

Photosynthesis is a natural phenomenon of photocatalytic reduction for carbon dioxide. It is a key project to achieve the artificial photoreduction of  $\text{CO}_2$  using photocatalysts in the field of catalysis. It is not only an effective way to improve ecological circulation, but also an important way to put in practice of biomimetic synthesis. As we know, this photoreduction utilizes both the clean solar energy and the source of  $\text{CO}_2$  waste which gives rise to the environmental pollution and the greenhouse effect. Nanometer-sized semiconductors have high catalytic activities because of their obvious quantum effect. Moreover their optical response can be adjusted by the particle size, therefore the nanometer-sized semiconductors have recently been used as high effective photocatalyst for exploiting the solar energy. Based on the consideration mentioned above, in this dissertation, a critical review of the development of researches in these fields is given and the content of this work has been proposed. Adopting the coordination transformation method, which was firstly presented by our group, to prepare nanometer-sized photocatalysts  $\text{MS}(\text{M}=\text{Cd}, \text{Zn})$ , the principle and the kinetics of preparation, the dependence of the structure upon the preparation conditions, the mechanism and influence factors of photocatalytic reduction of carbon dioxide were investigated.

Nanometer-sized sulfides MS (M=Cd, Zn) were prepared by the coordination transformation method. Some polar polymers including chitosan (CTN), polyvinyl alcohol (PVA), polyethylene oxide (PEO) and polyacrylonitrile (PAN) were selected as polymer ligands to be coordinated with metal ions  $M^{2+}$  (M=Cd, Zn) and the polymer-metal complexes were then transformed to nanometer-sized semiconductors MS through introducing Na<sub>2</sub>S solution as the sulfide source. By analyzing the principles, researching on the kinetics of the process, and characterizing the structures and the dimension of MS particles, the universality of this method for preparing nanometer-sized materials was demonstrated. The kinetics of preparation of the nanometer-sized MS particles, which was carried out by an indirect chromogenic measurement to determine the variation of the concentration of sulfide ions, has been developed. According to the Fick's first diffusion law, the kinetics equations were established based on a mathematical simulation of the diffusion process with a non-constant source, and especially, accompanying chemical reactions taking place. The simulated curve is in good agreement with the experimental results. The diffusion coefficient  $D$  of sulfide ion in PVA-Zn<sup>2+</sup> complex film is  $9.92 \times 10^{-6} \text{ cm}^2/\text{s}$  by combining the kinetics equation and the experimental data. The constant of reaction rate and the active energy of the transformation from PVA-Zn<sup>2+</sup> complex to ZnS particles are 16.1 mol/L·s and 61.7 KJ/mol, respectively. According to the kinetics results, it was proposed that the size of the nanoparticles obtained by coordination transformation method can be predicted. The nanocrystallite size is

proportional to the degree of polymerization of the polar polymer and inversely proportional to the coordination number. It was found that the predicted results coincide with the measurement values.

From the IR spectra tracing the process, coordination bond was also found between the polymer and the nanometer-sized MS particles obtained by the coordination transformation method. The mechanism of the process was then proposed. The dominant crystallites of MS particles are demonstrated to be sphalerite structure by X-ray diffraction analysis. And their size is demonstrated to be in the nanoscale since the band-edge wavelength is considerably blue shifted in UV absorption spectra and the diffraction lines are obviously broadened in XRD patterns. It is implied that coordination transformation method can be used to prepare homogeneous, size controllable and stable nanoparticles. In addition, the particulate size was determined by XRD, TEM and UV spectroscopy, respectively. Among the different ways for evaluating the size of the nanoparticles, the value obtained by EMA (effective-mass approximation) method is close to that obtained by TEM, while the value by Scherrer equation based on XRD is obviously smaller than that by TEM. It is manifested that the polymers containing strong-coordination groups have better behavior to protect nanoparticles than those with only poor coordination groups. It is shown that the bigger the coordination number, the more the blue shift of the band edge absorption, the smaller the particle size should be. Small particles with great amount of blue shift were also obtained under low concentration of  $\text{Na}_2\text{S}$

solution, short time of the complex film dipping in the Na<sub>2</sub>S solution and low temperature of the transformation reaction. But the concentration and the dipping time only in a certain range would affect the size of the nanoparticles.

The photocatalysts of SiO<sub>2</sub>/PVA/MS was prepared by coordination transformation method with silica supporter. The photoreduction of CO<sub>2</sub> induced by photocatalysis was investigated. The gas chromatogram of the photocatalytic products indicated that there was oxygen produced. The main products catalyzed by nanometer-sized ZnS were methanol, ethanol, formaldehyde and a little nitromethane. The maximum amount of 10<sup>-4</sup> mol/(0.1gCat24h) of the organic products was obtained. Meanwhile the main products catalyzed by nanometer-sized CdS were methanol, formaldehyde and a little nitromethane. The amount was 10<sup>-5</sup> mol/(0.1gCat24h). In the presence of Na<sub>2</sub>SO<sub>3</sub> reactant the yield of organic compounds would increase and there was a lot of acetaldehyde produced in the system. It indicated that the catalytic ability of nanometer-sized photocatalyst CdS is weaker than that of nanometer-sized ZnS, and that the ability, however, would be enhanced by reductants. Based on the resultants and the characteristics of the volume change of the system, the photocatalytic mechanism of reduction of CO<sub>2</sub> catalyzed by nanometer-sized MS supported by silica was suggested. Electron-hole pairs were generated by photos, and the current carrier transferred to CO<sub>2</sub> (or HCO<sub>3</sub><sup>-</sup>) and H<sub>2</sub>O, respectively, therefore a series of redox reactions were induced to form formic acid, formaldehyde and methanol, and so on. XPS showed that sulfur



atoms in the nanocatalysts participated in the reduction procedure. It was found that under different conditions of the preparation different structures of the nanocatalysts would be obtained, and then it results in different catalytic activities. With increasing the coordination number and/or decreasing the concentration of  $\text{Na}_2\text{S}$  solution, the catalytic activity of the nanometer-sized MS reveals an optimum value, but do not perform a monotone function of these parameters. Meanwhile, the excess of  $\text{S}^{2-}$  causing metal ion vacancies would facilitate the photoreduction of  $\text{CO}_2$  due to the strong electron donating ability of the sulfur anion. It is inevitable that the nanocatalyst MS would be photolysis accompanying with the photocatalysis, then the surface modification is important. Nanometer-sized sulfide catalysts modified by CuS show that the photocatalytic ability is enhanced and the life time of photocatalysis can be prolonged. On the other hand, the protecting effect do not get obvious improvement when ZnS was modified by ZnOH to form ZnO capper.

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**Key words** nanocrystalline, ZnS, CdS, polymer ligands, coordination transformation method, photocatalysis, reduction,  $\text{CO}_2$

## 目 录

第一章 前 言	1
1.1 概 述	1
1.2 聚合物/纳米(Zn,Cd)S 复合材料的制备	6
1.3 纳米 II-VI 族半导体能带结构	13
1.4 纳米半导体光催化性能	16
1.5 CO <sub>2</sub> 光催化还原	27
1.6 选题目的、意义及依据	37
1.7 研究内容	42
第二章 实验内容	45
2.1 实验仪器与药品	45
2.2 纳米 MS( M=Cd, Zn) 制备	46
2.3 纳米 MS( M=Cd, Zn) 制备动力学	48
2.4 纳米 MS( M=Cd, Zn) 结构表征	51
2.5 纳米催化剂的制备	53
2.6 催化剂结构表征	56
2.7 纳米 MS(M=Cd, Zn) 光催化性能	57
2.8 光催化反应产物气相色谱测定	59
第三章 纳米 MS 制备原理及动力学	61
3.1 配位转化法原理及应用	61
3.2 配位转化动力学研究	73
第四章 纳米半导体 MS(M=Cd,Zn)的结构	99
4.1 引 言	99



4.2 MS 形成机理 .....	103
4.3 晶体结构分析 .....	113
4.4 纳米硫化物尺寸表征 .....	120
4.5 光响应特性及其影响因素 .....	137
4.6 催化剂结构分析 .....	151
第五章 纳米 MS 的光催化 $\text{CO}_2$ 还原性能 .....	158
5.1 催化反应表征参数选择 .....	158
5.2 催化反应产物表征 .....	160
5.3 催化反应效率估算 .....	170
5.4 催化反应机理探讨 .....	175
5.5 催化反应过程及影响因素 .....	183
5.6 本实验催化体系特点 .....	201
5.7 未来研究方向 .....	204
第六章 结论 .....	207
参考文献 .....	212
附录 1 制备条件与粒径一览表 .....	234
致 谢 .....	237