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博 士 学 位 论 文

纳米结构无机半导体电沉积及其固态光伏电池

Electrodeposition of Nanostructured Inorganic Semiconductors and their Solid-state Photovoltaic Cells

冯 增 芳

指导教师姓名：林 仲 华 教授

周 剑 章 副教授

专 业 名 称：物 理 化 学

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冯增芳

指导教师

林仲华教授

周剑章副教授

厦门大学

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目　录

Table of Contents

摘 要

纳米结构无机半导体电沉积及其固态光伏电池

作为现代经济社会能源支柱的化石燃料将可能在本世纪消耗殆尽，能源的短缺和环境的恶化使得人们对清洁、可再生能源的需求越来越迫切。太阳能是一种取之不尽、用之不竭的绿色环保能源，太阳能电池是利用太阳能的有效途径，所以在最近几年里，传统硅基太阳能电池得到了极大发展。但是要大规模普及应用乃至取代传统能源，硅基太阳能电池仍然面临着较低性价比的问题；而造成该问题的根源在于其工作原理：这类太阳能电池的光生电子-空穴必须扩散至空间电荷区才能有效分离，这就要求有较长的载流子（电子/空穴）扩散长度（即寿命），于是带来了材料高纯度和完美晶型结构要求，导致半导体材料价格昂贵。这就决定了仅仅依靠传统太阳能电池材料和结构的改进以大幅降低成本是不现实的。在纳米结构太阳能电池中，光生电荷在光伏活性薄层中产生，主要依靠界面电荷转移分离光生电荷，对载流子扩散长度要求较低，因此可以利用价格比较低的半导体材料而降低电池成本。所以在最近的二十年，采用纳米技术制备不同纳米结构半导体电池成为太阳能电池研究的主流，其中染料敏化太阳能电池被认为是最有可能在较短时期内走向工业化生产的新型太阳能电池。但是它依然面临着以下几个问题：（1）有机染料的使用由于有机分子的稳定性不足带来了电池性能的稳定性和电池寿命问题，另外还存在染料价格问题。（2）电子/空穴在传输过程中，由于纳米粒子间存在大量晶界导致了光生电荷较低的传输效率，易发生反向复合。（3）液态电解质溶液带来了电池的封装问题和电解质渗漏，也带来了电池的稳定性和寿命问题。

为了尽可能地降低电池成本，本论文研究制备纳米结构半导体太阳能电池，围绕解决染料敏化太阳能电池中存在的以上三个问题进行探索并得到结果如下：

一、纳米结构半导体材料有特殊的光学、电学性质而可能具备优异的光电性能。而材料的结构、形状和性质与其制备方法密切相关。纳米半导体的制备方法多种多样。因为具有常温制备，与基底结合牢固，通过外加电压、电流等

沉积条件可精确控制反应速率、材料沉积量，并影响其微观结构和形状等优点，本论文主要采用电化学沉积方法制备不同纳米结构半导体材料。

1. 电沉积得到 ZnO 纳米棒、纳米管，Ⅱ-Ⅵ族半导体 CdS、CdSe、CdTe 纳米粒子；溶胶-凝胶法、热分解法分别制备 ZnO 纳米粒子；ZnO 纳米棒为牺牲模板制备 TiO_2 纳米管/棒。

2. 首次用无模板直接电沉积制备得到 CdS、CdSe、CdTe 的纳米线结构，研究其结构和光学性能等，并从其晶体结构和电化学沉积的成核及生长过程较为深入探讨这些纳米棒结构的沉积机理。

3. 电沉积得到 PbSe 的纳米片，制备出高度对称的立方体、八面体以及空间三维多级复杂纳米/微米结构。

二、为避免液态电解质溶液带来的电池封装问题和渗漏问题，本论文采用固态空穴传输材料：Nafion 基氧化还原聚合物和导电聚合物 PEDOT：PSS。其中，Nafion 基氧化还原聚合物是一种性能优良的空穴递体，因此首次将其应用在光伏电池中作为固态空穴传输材料。而 PEDOT：PSS 是一种常用的空穴传输材料。

三、引入直线电子传输概念，在 FTO 导电玻璃基底上制备 ZnO 纳米棒、纳米管，TiO_2 纳米管作为电子传输材料。发现由于晶界的减少和电子传输的一维限域，ZnO 纳米棒、纳米管确实有利于电子的传输，但是在 ZnO 纳米管结构中存在较多的表面态导致复合中心密度增大。而所制备的 TiO_2 纳米管由许多小晶粒聚集，为多晶结构，仍然存在着许多晶界，不利于电子的有效传输。

四、在上述工作的基础上，本论文以一维有序的 ZnO 纳米棒/纳米管、TiO_2 纳米管为电子传输材料，纳米结构无机半导体 CdS、CdSe、CdTe 代替有机染料作为光伏活性材料，Nafion 基氧化还原聚合物为固态空穴传输材料制备固态光伏电池。由于 CdS 光电响应范围窄、CdTe 存在较多的晶格缺陷等复合严重，所制备的光伏电池以 CdSe 为最佳，得到电池的光电转换效率超过 3%，表明 Nafion 基氧化还原聚合物可以应用在光伏电池中，是一种性能优良的固态空穴传输材料；该结构光伏电池有较好的应用潜力。

五、将所制备得到的 CdS、CdSe、CdTe 纳米线作为光伏活性材料（同时作为一维电子传输材料）、导电聚合物 PEDOT：PSS 为空穴传输材料制备固态光

伏电池。将 ZnO、TiO_2 等电子传输材料制备成一维纳米结构可以较好地解决电子的传输效率和电子回流引起的复合问题。但是就目前的制备技术，纳米结构的有序化必然带来比表面积的减小，影响电子和空穴的分离和传输效率；以及相应的光伏活性材料负载量的减少，导致光吸收不充分，从而导致电池性能提升有限。因此，采用光伏活性材料 CdS、CdSe、CdTe 的一维纳米线结构，这些纳米线结构同样能够提供较大的界面以利于光生电荷（主要是空穴）的分离，另外光伏活性材料的增加能实现良好的光吸收，纳米线结构由于散射增强也导致了紫光区和近紫外光区的吸收增强。最终，这些电池也获得了超过 3%的光电转换效率，由于同样的原因，仍是以 CdSe 纳米线光伏电池性能最佳。该结果说明，将光伏活性材料而不是 ZnO、TiO_2 等制备成一维纳米有序结构，也是制备纳米结构太阳能电池的一个有效思路。

关 键 词

纳米半导体； 电沉积； 光伏电池

Abstract

Electrodeposition of Nanostructured Inorganic Semiconductors and their Solid-state Photovoltaic Cells

The mainstay of energy sources, coal、oil and natural gas will be depleted someday in the future. The energy shortage and the environmental pollution induced by the fossil fuels makes the demands of a clean, renewable energy sources more and more urgent. Solar energy is an inexhaustible and green energy; solar cell is an effective way in solar energy utilization. Consequently, the traditional silicon solar cells got a great development in recent years. But the relative high cost is still the blockage for the solar cells in achieving widespread application and even replace the traditional energy. But the problem lies in its working principle: the photo-generated electrons and holes must diffuse to the space charge region at the interface where they are separated, which requires a long diffusion length of electrons/holes. As a result, the materials should be with high purity and perfect crystal structure, which results in the high production costs of semiconductor materials. The drastic reduction of the solar cell cost cannot be expected by using the conventional materials and solar cell structures. While in nanostructured solar cells, the separation of the photo-generated electrons and holes, rely mainly on the interface charge transfer, demanding shorter diffusion length of electrons/holes. Therefore it can use the low cost semiconductor materials and the induced lower cost of solar cells. So in recent 20 years, several nanostructured solar cells using various nanostructures semiconductors are developed. Among with, the dye-sensitized solar cells (DSSCs) are believed to be the most likely to industrialized production in a short period. But there are still some problems: (1) the use of organic dyes, the instability of organic molecules induces the instability of the cells; additionally the dyes are usually expensive. (2) In nanoparticles layer, the electronic/hole transport rate is usually low as the large number interfaces, and the backflow of electrons causes recombination. (3) Liquid electrolytes brought the difficulty in package and the inevitable leakage also causes the instability of the cells.

To reduce the cell costs, here we fabricated some nanostructured photovoltaic cells to solve the three problems in DSSCs, and the results were showed as follows:

1. Nanostructure semiconductor materials may have special optical and electrical properties and the outstanding performance in photoelectric conversion. The structure and the induced properties of materials are closely related to the preparation. There are various preparation ways of nanostructured semiconductors. As electrochemical deposition method has the advantages of lower temperature, the intense attachment to the base, conveniently and accurately control of the deposition rate, the quantity, and the nanostructures through the applied voltage, current, etc. Electrodeposition was mainly used in preparation of nanostructured semiconductor materials.

(1) Electrodeposition of ZnO nanorods、nanotubes, Ⅱ-Ⅵ semiconductors of CdS CdSe CdTe nanoparticles; fabrication of ZnO nanoparticles with sol-gel and thermal decomposition method; fabrication of TiO_2 nanotube/nanorods with sacrificial template of ZnO nanorods.

(2) Template-free electrodeposition of CdS、 CdSe、 CdTe nanowires for the first time. Their structure and optical properties were studied and the growth mechanism was discussed from the crystal properties and the electrochemical in nucleation and growth process.

(3) With the method of electrodeposition, PbSe nanosheets, high symmetric cube, octagonal and multilevel complex three-dimensional structures of nano/microns were obtained.

2. To avoid package and leakage problems from the liquid electrolyte, two kinds of solid-state hole-transporting materials were used: Nafion-base redox polymers and conductive polymers PEDOT：PSS. Nafion-base redox polymer was first applied in photovoltaic cells as solid hole-transporting materials. And PEDOT：PSS is a kind of hole-transporting materials in common use.

3. According to line electron transport, ZnO nanorods/nanotubes and TiO_2 nanotubes were deposited on the FTO substrates as the electron transporting materials. The nanostructures of ZnO nanorods/nanotubes were beneficial to the electron transporting. While in ZnO nanotubes, there are more surface states which increased the recombination center, and TiO_2 nanotubes were the aggregation of crystal grains, there are still a lot of interfaces which blocks the electron transport.

4. On the basis of the previous work, one-dimensional ZnO nanorods/nanotubes, TiO_2 nanotubes were used as electron-transporting materials; instead of organic dyes, nanostructured semiconductors of CdS, CdTe CdSe as light-harvesting material; and Nafion base redox polymer as hole-transporting materials to fabricate solid-state photovoltaic cells. Due to the relative large bandgap of CdS and the exist of defects in CdTe, the photoelectric response in the two materials are poor, the photovoltaic cells with CdSe obtained an overall energy conversion efficiency over 3%. The Nafion-base redox polymer was turned out to be an attractive solid-state hole-transporting material. These photovoltaic cells are of considerable potential for practical application.

5. One-dimensional nanostructures can well improve the electron transporting and avoid the electron backflow. With available synthesis method, the orderly nanostructures will bring the decrease of surface(i.e., the interface where the electrons/holes were separated), and the corresponding decrease of light-harvesting material, causes inadequate light absorption, leading to the little improvement. Therefore, CdS CdSe, CdTe nanowires was used as light-harvesting material, conductive polymers PEDOT: PSS as hole-transport materials to prepare solid-state photovoltaic cells. These new nanowires structures can also provide larger interface, the increase of the light harvesting materials can realize good light absorption, the scattering in nanowires resulted in an increase the absorption in violet and near ultraviolet lights. Finally, these cells also received an overall energy conversion efficiency over 3%. The results show that it may be an effective way to fabricate photovoltaic cells with one-dimension orderly nanostructured light-harvesting material, instead of ZnO, TiO_2.