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硕 士 学 位 论 文

铝电解电容器用低压阳极箔复合氧化膜  
及PbS纳米棒的制备

Preparation of Composite Films on Low Voltage Anode Foil for  
Aluminum Electrolytic Capacitors and PbS Nanorods

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**Preparation of Composite Films on Low Voltage Anode Foil for  
Aluminum Electrolytic Capacitors and PbS Nanorods**



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**Master of Science**

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## 摘要

本论文工作由两部分组成：一部分是铝电解电容器用低压阳极箔复合膜的制备；另一部分是 PbS 纳米棒的制备。

### （ I ）铝电解电容器用低压阳极箔复合膜的制备

铝电解电容器具有单位体积电容量大、重量轻、体积小、价廉等特点，应用广泛，是大量使用的、不可取代的电子元件之一。然而，由于难以在电路中集成，其体积制约了电子系统的小型化进程。电极箔是铝电解电容器制造的重要原材料，高比容铝电极箔的研制是实现铝电解电容器小型化的关键。当电压一定时，提高阳极箔比容有以下两种途径：（1）扩大阳极箔表面积  $S$ ；（2）提高电介质的相对介电常数  $\epsilon_r$ 。通过扩大阳极箔表面积  $S$  来提高比容的技术目前已基本达到极限，而在铝阳极箔表面生长高介电常数复合氧化膜的技术为提高铝电极箔的比容提供了新的途径。

本工作旨在采用电化学方法在铝电解电容器用低压阳极箔表面制备高介电常数的  $\text{Al}_2\text{O}_3\text{-TiO}_2$  复合氧化膜，优化电化学沉积参数和热处理温度，大幅度提高铝电极箔的比容。主要研究进展及结果如下：

1. 应用电泳沉积技术，在分散有  $\text{TiO}_2$  纳米颗粒的含有  $\text{I}_2$ -水-丙酮的异丙醇溶液中，在低压阳极箔表面成功制备了高介电常数的  $\text{Al}_2\text{O}_3\text{-TiO}_2$  复合氧化膜。发现阳极箔在  $\text{pH}=2\sim 5$  的以异丙醇（水-丙酮- $\text{I}_2$  为添加剂）为溶剂的  $\text{TiO}_2$  悬浮液中，采用  $20\text{ V}$  电压电泳沉积  $3\text{ min}$ ，经过  $550\text{ }^\circ\text{C}$  热处理  $10\text{ min}$ ，最后经化成处理后具有最高的比容，比未沉积  $\text{TiO}_2$  的样品的比容提高了约  $20\%$ 。
2. 应用电解沉积技术，以纯钛为牺牲阳极、腐蚀箔为阴极，在碘的丙酮溶液中将  $\text{Ti}$  物种沉积于低压阳极箔表面，样品经热处理和化成后表面获得了  $\text{Al}_2\text{O}_3\text{-TiO}_2$  复合氧化膜。发现在含有  $2.5\times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$  碘的丙酮溶液中在  $50\text{ V}$  电压下沉积  $3\text{ min}$ ，然后通过经  $550\text{ }^\circ\text{C}$  热处理  $30\text{ min}$ ，最后经化成处理后制得的样品比未沉积  $\text{TiO}_2$  的样品的比容提高约  $20\%$ 。
3. 两种方法制得的阳极箔均具有较好的升压降流性质，大大节省了化成时间，具有一定的工业化应用前景。

## (II) PbS 纳米棒的制备

PbS 作为 IV-VI 族半导体材料中的重要一员, 具有窄的禁带宽度 (0.41 eV) 和大的波尔半径 (18 nm), 即使是较大的纳米颗粒仍然具有量子尺寸效应。因其具有奇异的光学和电学性能, PbS 纳米材料被广泛地应用于红外探测器、太阳能电池和电致发光设备等领域。由于一维 PbS 纳米材料与三维材料中电子的转移不同, 一维 PbS 纳米材料的合成引起了科研工作者的极大兴趣。然而, PbS 属于立方岩盐矿结构, 具有三维各向同性, 因此, 制备各向异性的一维 PbS 纳米材料仍然是一个很大的挑战。

本工作旨在以三嵌段共聚物 P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) 为结构引导剂, 采用水热法制备 PbS 纳米棒。考察 P123 浓度、水热反应温度和硫源对反应产物形貌的影响, 并对其反应机理和光学性能进行研究。主要研究进展及结果如下:

1. 以 P123 为结构引导剂, 在含有  $\text{Pb}(\text{NO}_3)_2$  和硫脲的水溶液中于 100 °C 下通过水热反应成功制备了直径在 40~70 nm, 长度为 200~600 nm 的 PbS 纳米棒。XRD 和 HRTEM 证实了 PbS 纳米棒为高度结晶的晶体, 生长方向为  $\langle 111 \rangle$ 。
2. PbS 纳米棒 UV-Vis 漫反射光谱显示其带边相对于块体 PbS 略有蓝移, 具有潜在的光电应用价值。这种合成方法为其它一维纳米材料在 P123 水溶液中的合成提供了指导。

**关键词:** 铝电解电容器; 阳极箔; 复合氧化膜; PbS 纳米棒; 光学性能

## Abstract

This work consists of two parts: one is the preparation of composite films on low voltage anode foil for aluminum electrolytic capacitors, the other is the preparation of PbS nanorods.

### ( I ) Preparation of Composite Films on Low Voltage Anode Foil for Aluminum Electrolytic Capacitors

Aluminum electrolytic capacitors are widely used due to the characteristics of high capacitance and the ability to sustain high voltages, low cost, and convenient production, and is one of the largely used and irreplaceable electronic components. However, the miniaturization process of electronic systems is restricted by its big volume because it is difficult to integrate into the circuit. Aluminum anode foil is the material in the manufacture of aluminum electrolytic capacitors, while the preparation of aluminum anode foil with higher specific capacitance is a key to speed up the miniaturization process of the aluminum electrolytic capacitors. There are two ways to increase the specific capacitance when the voltage used in the anodizing is constant. The first way is to enlarge the surface  $S$ . The other way is to increase the relative dielectric constant  $\epsilon_r$ . At present, the increase of the specific capacitance by enlarging the surface  $S$  is near the end. The technique to prepare the composite oxide film with high dielectric constant on the surface of anode foil gives a new route to increase the specific capacitance of the aluminum foil.

The main goal and motivation of the present work is to prepare the  $\text{Al}_2\text{O}_3\text{-TiO}_2$  composite oxide film with high dielectric constant by the electrochemistry method used in low-voltage aluminum electrolytic capacitors. Through optimizing the electrochemical parameters and annealing temperature, the specific capacitance of aluminum anode foil could be increased significantly. The main results and progress of this work are outlined as following:

1.  $\text{Al}_2\text{O}_3\text{-TiO}_2$  composite oxide film on the surface of low-voltage aluminum anode

foil were prepared successfully by electrophoretic deposition in the isopropyl alcohol solution which consists of  $I_2$ ,  $H_2O$ , acetone and  $TiO_2$  nanoparticles. It was found that the aluminum anode foil obtained by electrophoretic deposition at 20 V for 3 min in the  $TiO_2$  suspension with the pH between 2 to 5, then annealing at 550 °C and finally anodizing at 20 V exhibited the highest specific capacitance which is about 20 % higher than those with pure etched aluminum foil specimens.

2. Ti species were deposited on the surface of low-voltage aluminum anode foil by cathodic electrodeposition in  $I_2$ -dissolved acetone solution using a Ti as a sacrificial anode and aluminum etched foil as a anode. Once being annealed and anodization, the  $Al_2O_3$ - $TiO_2$  composite oxide films were formed on the surface of low-voltage aluminum anode foil It was found that the aluminum anode foil obtained by electrodeposition at 50 V for 3 min in 2.5 mM  $I_2$ -acetone solution, then annealing at 550 °C and finally anodizing at 20 V exhibited about 20 % higher specific capacitance than those with pure etched aluminum foils.
3. The specimens prepared by both of above two methods have a good property of voltage and current along with the anodizing, which shortens the formation time and has the promising industrialized application prospect.

## ( II ) The Preparation of PbS Nanorods

PbS, as an important IV-VI semiconductor, is an attractive sulfide semiconductor with a narrow direct band gap of 0.41 eV and a large excitation Bohr radius of 18 nm, which permits size-quantum confinement effects to be clearly visible even for the large particles. With novel and excellent optical and electronic properties, nanoscaled PbS has been widely used for IR detectors, solar cells and electroluminescent devices. As the properties of one-dimensional (1D) PbS are substantially different from three-dimensional (3D) systems due to the change in the degree of charge carriers, the synthesis of 1D PbS has attracted much interest. However, PbS is a cubic rock salt structure, which is 3D isotropic. In contrast to the synthesis of isotropic systems, the preparation of anisotropic PbS nanocrystals remains a major challenge.



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