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高度有序介孔TiO_2薄膜的介观结构及其光生阴极保护性能研究

Investigations on Mesostructure and Photogenerated Cathodic Protection Properties of Highly-Ordered Mesoporous Titania Thin Films

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摘 要

介孔TiO_2薄膜由于其独特的有序孔道结构和高比表面积特性，已受到越来越多学者的关注，并广泛应用于一系列涉及光电化学反应的研究领域。由于薄膜内部纳米粒子的排布结构与材料的吸附性能、电子传输效率有着密切联系，薄膜制备过程中结构的调控显得尤为重要。因而，有必要对介观结构的表征和形成机理进行深入研究。此外，尽管介孔TiO_2薄膜材料在染料敏化太阳能电池、光催化和自清洁玻璃等方面的应用已经有了一定程度的发展，但其在光生阴极保护方面的研究尚未有人涉及。

本文基于蒸发诱导自组装结合溶胶-凝胶技术原理，以TBT-P123-BuOH-HCl混合液为前驱体溶胶，采用提拉法在高湿度环境下制得TiO_2湿膜，最终经过特殊的热处理工艺获得有序介孔TiO_2薄膜。结合电子显微观察、X射线衍射、吸附测试等表征手段，深入研究了热处理温度对薄膜介观结构演变和吸附润湿性能的影响，初步提出了介孔TiO_2薄膜的自组装和结构转变机理。同时，采用光电化学测试技术对介孔TiO_2薄膜的光生阴极保护性能进行了研究，进一步阐明了介观结构对材料光电性能的影响，主要研究内容和结果如下：

1、利用溶胶-凝胶提拉法在FTO导电玻璃上制备了有序介孔TiO_2薄膜，发现经 350 °C热处理后，薄膜内部的介孔呈三维六方对称排列($P6_3/mmc$空间群)；随着热处理温度升高至 450 °C~500 °C，孔洞沿着垂直基底的方向“首尾相连”形成类似网状的垂直孔道结构；与三维六方结构相比，垂直孔道结构对溶液分子表现出更加优秀的吸附和润湿性能。

2、探讨了薄膜介观结构的自组装和转变机理。研究表明：高湿度环境和低 TBT/P123 体积比是获得三维六方介观相的关键；同时热处理过程中，介孔沿着垂直方向的收缩合并及纳米晶粒的逐渐长大，是垂直孔道结构转变的主要原因。

3、研究了提拉速率对介孔TiO_2薄膜光生阴极保护性能的影响。结果显示：当提拉速率为 100mm/min时，TiO_2薄膜的厚度达到最大值，在光照下对 304 不锈钢起到最佳的光生阴极保护效果。

4、研究了介观结构对介孔TiO_2薄膜光生阴极保护性能的影响。光电化学测试结果表明：垂直孔道结构能显著提高光阳极对空穴捕获剂分子的吸附及光生电子的快速导

出，使材料表现出明显增强的光电性能。

关键词：蒸发诱导自组装；结构转变；垂直孔道(网状)结构；有序介孔TiO_2薄膜；吸附性能；光生阴极保护

Abstract

Mesoporous TiO_2 thin films have attracted much attention from researchers due to their ordered pore structures and properties of high surface area. And these materials are widely applied in the fields involving photoelectric chemical reaction. The structure tailoring during synthesis process is very important since the adsorption capacity and electron transmission efficiency of mesoporous TiO_2 films is greatly influenced by the geometrical arrangement of nanoparticles inside the thin films. Therefore, the deeper research on characterization and formation mechanism of mesostructure shows a high demand for actual applications. And now, mesoporous TiO_2 fims have got a developed study in many areas such as dye-sensitized solar cells, photocatalysis and self-cleaning coatings. However, so far as we know, no reports have been made on the photogenerated cathodic protection of such films.

In the present thesis, the synthesis strategy was based on evaporation induced self-assembly (EISA) combined with dip-coating method. The TBT-P123-BuOH-HCl precursors were dip-coated under high relative humidity condition onto the FTO substrates and underwent a special heat-treating process to form the highly ordered mesoporous TiO_2 fims. The effects of calcination temperature on the mesostructural transoformation, surface adsorption and wettiablity were investigated through the electron microscopy, diffraction patterns and adsorption-desorption tests. The mechanisms of self-assembly and structural transformation were preliminarily proposed. Meanwhile, the photogenerated cathodic protection property of mesoporous TiO_2 photoanode was also investigated through the photoelectrochemical measurement and the effect of mesostructure on the photoelectric property was further demonstrated. The main contents and results of this work were summarized as follows:

1. Highly ordered mesoporous TiO_2 films were successfully prepared on the FTO substrates by sol-gel dip-coating technique. And it was found that the thin films exhibited 3D hexagonal mesostructure (space group is $P6_3/mmc$) after calcinations at 350 ^oC. With increasing calcination temperature to 450~500 ^oC, the mesopores were connected

"end-to-end" along the perpendicular direction, forming a "Grid-like" mesostructure with orthogonal channels. Comparing with the 3D hexagonal mesostructure, the vertical channel-like mesostructure promoted the accessibility and wettiablity of solution molecules.

2. The mechanisms of self-assembly and structural transformation were investigated. And it was revealed that the high relative humidity atmosphere and low TBT/P123 Volume ratio were crucial for the formation of 3D hexagonal symmetry. Moreover, the 3D hexagonal mesostructure was transformed to the grid-like mesostructure with perpendicular porosity through the pore merging along perpendicular direction and the crystallites growth within the pore walls

3. The effect of pulling speed (in a dip-coating process) on the photogenerated cathodic protection property of mesoporous TiO_2 photoanode was investigated. The obtained results indicated that the thickness of TiO_2 films reached the maximum value at 100mm/min and the most effective photogenerated cathodic protection for 304SS were achieved under irradiation condition.

4. The effect of mesostructure on the photogenerated cathodic protection property of mesoporous TiO_2 photoanode was also investigated. It was deduced from the photoelectrochemical test that the mesostructure with perpendicular channels could facilitate the adsorption of hole-scavenging electrolyte and the transport of photo-excited electrons along the organized pore walls, which greatly enhanced the photoelectric property of highly ordered mesoporous TiO_2 photoanode.

Keywords: EISA; Structural transformation; Vertical grid-like structure; Ordered mesoporous TiO_2 film; Accessibility; Photogenerated cathodic protection

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