学校编码：10384　　　　　　　　　　　　分类号______密级__内部__

学号：20520061151960　　　　　　　　　　　　　　　UDC________

厦门大学

硕　士　学　位　论　文

碳载高指数晶面结构铂纳米晶的合成及其电催化性能研究

Synthesis of high-index faceted Pt nanocrystals supported on carbon black and investigation of their electrocatalytic property

黄志忠

指导教师姓名：孙 世 刚 教 授

周 志 有 副教授

专 业 名 称：物 理 化 学

论文提交日期：2009 年 10 月

论文答辩时间：2009 年 10 月

学位授予日期：2009 年 　月

答辩委员会主席：__________

评　　阅　　人：__________

Synthesis of high-index faceted Pt nanocrystals supported on carbon black and investigation of their electrocatalytic property

A Dissertation Submitted to the Graduate School of Xiamen

University for the Degree of

Master of Science

By

Zhi-Zhong Huang

This work was carried out under the supervision of

Prof. Shi-Gang Sun

Associate Prof. Zhi-You Zhou

At

Department of Chemistry, Xiamen University

Octorber 2009

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 2012 年 11 月 1 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

摘 要

负载到碳基底上的铂族金属纳米粒子是直接醇类燃料电池 (DAFC) 难以替代的催化剂。以单晶面为模型催化剂的基础研究指出铂族金属高指数晶面由于含有高密度的台阶原子和扭结原子，其催化活性和稳定性明显优于{111}、{100}等低指数晶面。但是，由于高指数晶面具有很高的表面能，一般的方法很难制备由高指数晶面围成的铂纳米催化剂。

本论文运用我们研究组发展的金属纳米晶体表面结构控制和生长的电化学方波电位法，通过优化制备条件，以Vulcan XC-72碳黑为载体制备了小粒径(与商业催化剂相当) 、具有高指数晶面结构的Pt/C纳米晶催化剂（HIF-Pt/C）。此外，我们还初步探索了高指数晶面结构的Rh纳米晶体的制备条件。获得的主要结果如下：

1. 在室温下制备前驱体Cs_2PtCl_6纳米粒子，用方波电位法合成了HIF-Pt/C (I)催化剂。合成的Pt纳米粒子为二十四面体纳米晶，平均粒径为76.7 nm。

2. 以聚乙二醇20000作保护剂，在室温下制备前驱体Cs_2PtCl_6纳米粒子，用方波电位法合成HIF-Pt/C (II)催化剂。合成的Pt纳米粒子为二十四面体纳米晶，平均粒径为9.9 nm。高氯酸溶液中的氧还原（ORR）的实验结果表明：HIF-Pt/C (II)催化剂对ORR的质量比活性比商业Pt/C催化剂要差，但面积比活性跟商业Pt/C催化剂相当。

3. 用液氮冷却法制备前驱体Cs_2PtCl_6纳米粒子，用方波电位法合成了HIF-Pt/C (III)催化剂。合成的Pt纳米晶的平均粒径为5.1 nm，Aberration-corrected HRTEM和循环伏安证实Pt纳米晶表面具有高密度的台阶原子。实验检测到HIF-Pt/C(III)对乙醇电氧化的催化活性以及使乙醇氧化生成CO_2的选择性都比商业Pt/C催化剂提高了一倍多。此外，HIF-Pt/C (III)的电化学稳定性还显著高于商业Pt/C催化剂。

4. 用液氮冷却法并以聚乙二醇20000作保护剂制备前驱体Cs_2PtCl_6纳米粒子，运用方波电位法得到HIF-Pt/C (IV)催化剂。合成的Pt纳米晶的平均粒径为2.8 nm，循环伏安结果显示其表面也具有高密度的台阶原子。

5. 运用方波电位电沉积法制备Rh纳米粒子。通过改变方波的上、下限电位，调控Rh纳米粒子的形状及表面结构。结果发现，只有方波上限电位高于1.00 V时，Rh金属表面才能发生较显著的氧吸附，得到非球形Rh纳米粒子，如枝状的Rh纳米粒子，五重孪晶结构的Rh纳米棒。

本文所研制的小粒径、具有高指数晶面结构碳载铂纳米晶催化剂不仅活性高而

且稳定性好，在燃料电池和其它各种电催化应用中具有重要的运用前景。

关键词： 铂族金属；高指数晶面结构纳米晶催化剂；Pt/C 催化剂；乙醇电氧化；电化学稳定性

Abstract

Platinum-group metal nanoparticles supported on carbon are the irreplaceable catalysts in direct alcohol fuel cells (DAFC). Fundamental studies of single-crystal model catalysts have demonstrated that high-index faceted platinum-group nanocrystals with high density of atomic steps and kinks usually exhibit much higher catalytic reactivity and stability than those of low-index {111} and {100} facets. However, due to high surface-energy of high-index factes, it is rather challenging to synthesize high-index faceted Pt nanocrystal catalysts by conventional methods.

In this thesis, we successfully apply an electrochemical square-wave potential method to prepare carbon-black-supported high-index faceted Pt nanocrystal catalysts （HIF-Pt/C） with a comparable size to commercial Pt/C catalysts. Besides, we preliminarily explored preparation conditions of high-index faceted Rh nanocrystals. The main results are listed below.

1. We have synthesized HIF-Pt/C (I) catalysts by employing electrochemical square-wave potential method to treat Cs_2PtCl_6 precursor prepared at room temperature. Pt nanoparticles are tetrahexahedral nanocrystals with an average size of 76.7 nm.

2. We have synthesized HIF-Pt/C (II) catalysts by employing electrochemical square-wave potential method to treat Cs_2PtCl_6 precursor prepared at room temperature with polyethylene glycol 20000 as capping agent. Pt nanoparticles are tetrahexahedral nanocrystals with an average size of 9.9 nm. The experimental results of the oxygen reduction reaction（ORR） in perchloric acid demonstrate that HIF-Pt/C (II) catalysts exhibit lower mass activity than commercial catalysts as well as the same specific activity toward ORR.

3. We have synthesized HIF-Pt/C (III) catalysts by employing electrochemical square-wave potential method to treat Cs_2PtCl_6 precursor prepared with liquid nitrogen cooling method. The experimental results of aberration-corrected HRTEM and cyclic voltammograms indicate that Pt nanocrystals with an average size of 5.1 nm possess a high density of atomic steps. Electrocatalytic tests of ethanol oxidation demonstrate that the HIF-Pt/C (III) catalysts exhibite catalytic activity and selectivity to CO_2 at least 2

times higher than those of commercial Pt/C catalysts. Furthermore, HIF-Pt/C (III) catalysts exhibite obviously higher electrochemical stability than that of commercial Pt/C catalysts.

4. We have synthesized HIF-Pt/C (IV) catalysts by employing electrochemical square-wave potential to treat Cs_2PtCl_6 precursor by combining liquid nitrogen cooling method with polyethylene glycol 20000 as capping agent. The experimental results of cyclic voltammograms indicate that Pt nanocrystals with an average size of 2.8 nm also possess a high density of atomic steps.

5. Rh nanoparticles are prepared by square-wave potential electrodeposition. It has been demonstrated that the shape and surface structure of Rh nanoparticles can be altered by varying the lower (E_L) and upper (E_U) limit of the square-wave potential. It has shown that only when the E_U is higher than 1.00 V, non-spherical Rh nanoparticles such as branched Rh nanoparticles and five-fold twinned Rh nanorods occur by significant oxidation-reduction-induced growth.

High-index faceted Pt nanocrystals with small size supported on carbon black exhibite enhanced catalytic activity and stability, and will be used as promising catalysts applied in fuel cells and a variety of other electro-catalytic applications.

Keywords: Platinum-group metals; high-index faceted nanocrystal catalysts; Pt/C catalysts; ethanol electrooxidation; electrochemical stability

目 录

Table of contents