学校编码：10384　　分类号＿＿＿＿密级＿＿

学号：　20520131151643　　UDC＿＿＿＿＿

厦门大学

硕　士　学　位　论　文

高指数晶面结构 Cu 纳米晶的电化学制备及其电催化 CO_2 还原性能研究

Electrochemical Synthesis of Copper Nanocrystals with High-Index Facets and Investigation of Their Performance over Electrochemical Reduction of CO_2

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论文提交日期：2016 年　5 月

论文答辩时间：2016 年　5 月

学位授予日期：2016 年　　月

答辩委员会主席：＿＿＿＿＿

评　　阅　　人：＿＿＿＿＿

2016 年 5 月

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A Dissertation Submitted to the Graduate School of Xiamen University for the Degree of

Master of Science

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At

Department of Chemistry, Xiamen University

May, 2016

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摘要

铜在自然界中储量丰富，具有优良的导电性、催化性能，并且与 Pt、Pd、Au、Ag 等贵金属相比非常廉价，在很多领域拥有众多潜在应用价值。随着温室效应的加剧，如何更好地将 CO_2 转化成能源具有非常重要的现实意义，铜是唯一一种可将 CO_2 还原成 CH_4 和 C_2H_4 等碳氢化合物且具有较高选择性的金属，利用铜基纳米材料电催化 CO_2 还原是当今研究的热点，电催化 CO_2 还原的反应作为表面催化反应的一种，其催化活性和选择性强烈依赖于催化剂的电子结构和表面结构，即催化剂的组成和形貌，因此制备出具有特定晶面围成的铜纳米粒子并研究其电催化 CO_2 还原的性能，为应对目前研究中的挑战提供了新的思路。

本论文成功制备了高指数晶面铜纳米催化剂，合成了铜二十四面体纳米晶，同时研究了其电催化 CO_2 还原的性能。取得的主要结果如下：

1）首次制备出高指数晶面结构的铜二十四面体纳米晶。在酸性条件下，通过电化学方波电位技术先合成 Cu 纳米粒子，然后再进行 Pb UPD 处理，首次成功在 GC 电极表面制备出由具有开放结构的{530}晶面围成的 Cu 二十四面体纳米晶；研究了铜二十四面体的生长过程与机理，结果表明 Pb UPD 是生成铜二十四面体的重要因素，Pb UPD 使得到的铜二十四面体形貌更完美，同时，Pb UPD 也可以作为表征 Cu 纳米粒子电化学活性面积的一个有力手段，以计算 CO_2 还原实验中得到催化还原的电流密度；

2）铜二十四面体电催化 CO_2 还原的研究。采用线扫伏安法、恒电位电解还原法等方法来探究 Cu THH 电催化 CO_2 的催化活性和选择性，结果表明 Cu THH 对电催化 CO_2 还原具有一定的活性，但整体对碳氢化合物和液相产物的选择性不高，同时，在反应过程中，纳米粒子的表面结构较难保持，将其用于电催化 CO_2 还原体系当中有待今后进一步发展和完善。

本论文运用电化学方波电位法和 Pb UPD 技术，首次制备了高指数晶面围

成的铜纳米晶，并研究了其电催化 CO_2 还原的活性和选择性，为探索运用电化学方波电位技术制备除贵金属以外的其他金属催化剂提供了新思路，同时为进一步研究铜基纳米材料电催化 CO_2 还原提供了有效参考。

关键词：铜纳米晶，高指数晶面，电催化 CO_2 还原，铅欠电位沉积

Abstract

Copper is abundant in nature, with excellent electrical conductivity, catalytic properties. It's cheaper compared to Pt, Pd, Ag, Au and other noble metals, so it is a good replacement in many potential areas. With the aggravation of the "greenhouse effect", how to make better use of CO_2 and transfer it into useful energy has very important practical significance. Copper is the only metal that can convert CO_2 into hydrocarbons such as CH_4 and C_2H_4 with higher selectivity, so use copper based nanomaterials for catalytic CO_2 reduction is a hotspot of current research. Electric catalytic reduction of CO_2 is one of the surface catalytic reactions, so its catalytic activity and selectivity strongly depends on the electronic structure and surface structure of catalyst, that is the composition and morphology of the catalyst. Therefore in order to meet the challenges of present studies, the shape-controlled synthesis of copper nanocrystals bounded by specific facets and study its performance for electrochemical reduction of CO_2 could be a new idea.

In this thesis, we successfully synthesized copper nanocrystals bounded by high-index facets, that is Cu tetrahexahedron (THH), and studied its performance of electrochemical reduction of CO_2. The main results are as following:

1) Tetrahexahedral Cu nanocrystals (THH Cu NCs) have been firstly prepared. First of all, Cu nanoparticles were synthesized by using electrochemical square-wave potential method, then Pb UPD on Cu nanoparticles were carried out, which result in the first synthesis of THH Cu NCs enclosed with {530} high-index facets on GC electrode surface. Moreover, we studied the growth process and formation mechanism of THH Cu NCs, the results show that Pb UPD on Cu is an important factor for the final THH shape. With the increase of Pb concentration, the Cu THH became more perfect and angular. Meanwhile, Pb UPD also can be used as a method to calculate the electrochemical surface area of Cu nanoparticles, which are used in calculating the current density of CO_2 reduction.

2) Studied the performance of electrochemical reduction of CO_2 on Cu THH. Through electrochemical methods, such as linear sweep voltammetry and potentiostatic electrolysis method,we explored the electrochemical catalytic activity and electrochemical selectivity for electrochemical reduction of CO_2. The results show that Cu THH has a certain catalytic activity for CO_2 reduction, but the selectivity of hydrocarbons and liquid product according to the overall product is not high,meanwhile, the surface morphology of the nanoparticles is a little difficult to maintain during the reaction process.Therefore, because of its structural instability, although theoretically Cu THH is an ideal catalyst for electrochemical reduction of CO_2, to use it for the system of electrochemical reduction of CO_2 remains to be further research.

This thesis use electrochemical square wave technology and Pb UPD process, prepared successfully Cu THH nanocrystals enclosed by high-index facets for the first time, and explored its catalytic activity and selectivity of electrochemical reduction of CO_2, providing a new approach for the preparation of metal nanocrystals other than noble metal nanocrystals through electrochemical methods,and at the same time, providing effective reference for further research of electrochemical reduction of CO_2 on copper based nanomaterials.

Keywords: copper nanocrystals, high-index facets, CO_2 electroreduction, Pb UPD

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