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厦门大学

硕 士 学 位 论 文

Fe 纳米粒子的电化学形状控制合成、结构表征与性能

Electrochemically shape-controlled synthesis of Fe nanoparticles, their structural characterization and properties

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论文提交日期：2009 年 8 月
论文答辩时间：2009 年 9 月
学位授予日期：2009 年 月

答辩委员会主席：_____
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_____

2009 年 8 月

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Electrochemically shape-controlled synthesis of Fe nanoparticles, their structural characterization and properties

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

By

Yan-Xin Chen

This work was carried out under the supervision of

Prof. Shi-Gang Sun

At

Department of Chemistry, Xiamen University

August 2009

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摘 要

一般来说，金属纳米催化剂的催化活性可以通过以下两个途径来提高：其一，改变金属纳米催化剂的成分，也就是通过改变化学组成和电子结构。其二，改变金属纳米粒子催化剂表面的原子排列结构，即通过调谐表面几何结构，后者可以通过形貌控制合成来实现。这也是当前纳米科技技术的一个重要的前沿研究领域。

电催化和多相催化反应都是表面反应，催化剂作用的关键是其表面原子与反应分子之间的相互作用。因此，若能通过形貌控制合成，制备出具有开放的表面原子排列结构的金属催化剂，将可以显著提高催化剂的活性和选择性。这将对催化剂的制备产生重要而深远的影响。

电化学方法具有独到的优势，被证明是一种实现纳米粒子形状控制合成的重要方法，该方法通常是在导电基底上，通过阴极还原制备金属纳米粒子或者薄膜，所得到的负载有金属的电极可直接用于电催化研究。该方法最大优点在于它能够通过改变沉积条件（成核电位，成核时间，生长电位，生长电位，沉积液浓度等），达到精确调节纳米晶体各个晶面生长速度的目的，进而获得由特定晶面组成的纳米材料。此外电沉积时由于金属纳米粒子被固定在电极表面，显著消除了团聚现象，镀液中可以不加稳定剂，这有利于催化性能研究。

本论文中，我们发展了金属纳米晶体表面结构控制和生长的程序电位阶跃电沉积方法，成功地实现了对 Fe 纳米晶体形状和表面结构的精确调控。取得的主要研究结果如下：

1.用循环伏安（CV）和恒电位（CA）电沉积的方法，在玻碳（GC）基底上制备具有立方体结构的 Fe 单晶纳米粒子，通过 SEM，HRTEM，XPS，XRD 等手段对其成分，形貌和结构进行了研究

2. 成功地通过试验条件的改变，对立方体形 Fe 单晶纳米粒子粒径的大小变化进行了控制，得到了一系列粒径分布的立方体形单晶 Fe 纳米粒子。

3. 对立方体形 Fe 单晶纳米粒子的生长机理和电催化活性进行了细致的研究。建立了对本体 Fe 电极和纳米 Fe 电极活化表面积的标定方法

4. 发展程序电位阶跃电沉积方法采用阶跃电位法，以玻碳（GC）为基底，通过对生长对电位的精确控制，系统地改变纳米粒子表面各种（hkl）密勒指数二维晶

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核的生长速度，实现了对 Fe 纳米晶体形状和表面结构的精确调控。成功地制备出具有完美晶型的菱形十二面体、四方双锥、一系列十八面体，以及立方体 Fe 单晶纳米粒子。

5. 对于制备的不同形貌单晶 Fe 纳米粒子的催化性能研究表明，Fe 单晶纳米粒子的催化性能与其表面开放程度 *R* 成正比关系。测得，在 0.2MNaOH+0.01MNaNO$_2$ 溶液中，-1.188V 处恒电位反应 200s 时，立方体形 Fe 纳米催化剂产生的稳态还原电流密度 j_{cube} 为-7.126 mA.cm^{-2}，约为相同试验条件下十八面体催化剂产生的稳态还原电流密度的 1.8～4.8 倍($j_{18\text{-facet polyhedra}}$ 为-3.985～1.486 mA.cm^{-2})；约为菱形十二面体/四方双锥的 27 倍（$j_{R\text{-}D}\approx j_{R\text{-}D}$ 都约为-0.26 mA.cm^{-2}）；约为本体 Fe 催化剂的 18 倍（$j_{bulk\text{-}Fe}$=-0.39 mA.cm^{-2}）。.

6. 采用程序电位阶跃电沉积法，以玻碳（GC）为基底，通过对成核电位和成核时间的调控，成功地制备出八极子、枝晶和平行连晶形单晶 Fe 纳米粒子。通过 SEM、STM 等技术对八极子的表面结构进行观察和表征，分析并提出其可能的生长模式。此外，通过运用 SEM 技术系统而详细地研究了枝晶和平行连晶形单晶 Fe 纳米粒子的生长过程，并运用 HRTEM 和 SAED 分析其晶面结构。研究结果表明，在对亚硝酸盐的电催化还原过程中，八极子和枝晶状 Fe 纳米催化剂表现出比立方体 Fe 更高的催化活性。

本论文发展的金属纳米催化剂表面结构控制和生长的程序电位阶跃电沉积方法，不仅制备出一系列不同形貌的 Fe 单晶纳米粒子，其研究结果还从实验上验证了二维晶核生长理论。该研究结果还显示出，在实现纳米催化剂形状控制与合成的征程中，电化学法是一种非常有效的方法。它为合成和制备更多、更高效的催化剂提供了有效的途径。

关键词： 形状控制合成；铁；纳米单晶；开放结构晶面；电催化

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Abstract

Catalytic performance of nanocrystals (NCs) can be finely tuned either by changing their composition, which mediates electronic structure, or by altering their shape, which determines their surface atomic arrangement and coordination. Therefore, the shape-controlled synthesis of nanocrystals presents an important way for tuning the activity, stability, and selectivity of nanocrystal catalysts.

Although a variety of well-defined shapes of metal NCs with enhanced optical, electronic, and catalytic properties have been synthesized in the past decade, most of them are bounded by closest-packing facets because of the limit of crystal growth rule, which necessitates a minimization of the surface energy of the NCs. As the closest-packed facets are composed of atoms with high coordination number and accordingly have a low surface energy, they are stable but in general exhibit low catalytic activities for chemical reactions. The synthesis of NCs bounded by crystalline facets with an open structure, i.e., with surface atoms of low coordination number and thus high surface energy, presents a promising direction in catalyst design and synthesis, although it is highly challenging

As the fourth most abundant element on earth. Fe NCs have been extensively investigated because of their wide applications. Especially Fe NCs are very important catalysts in denitrification, which is of very significant in today's society since the intensive use of fertilizers in agriculture and nitrates in some industries causes severe nitrate/nitrite pollution of water sources.

In this thesis, we have developed an programed potential-step method to control the surface structure and growth of Fe nanocrystals, and prepared successfully nanocatalysts of Fe bounded by {110} or {100}planes. The study has demonstrated that the electrocatalytic activity of the Fe NCs is enhanced by increasing the fraction of {100} facets on the Fe NC surface. The main results are as following:

1. Fe cuboid NCs supported on glassy carbon were prepared by electrochemical deposition under cyclic voltammetric (CV) and chronoamperometry (CA) conditions. The structure and composition of the Fe nanomaterials were characterized by scanning electron microscopy (SEM), selected area electron diffraction (SAED), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). The results demonstrated that the Fe

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cuboid nanoparticles are dispersed discretely on GC substrate, and the electrochemical synthesized nanocubes are single crystals of pure Fe.

2. The size of the cube Fe NCs can be controlled by varying the growth time and the $FeSO_4$ concentrations in solution.

3. The electrocatalytic activity of the synthesized Fe NCs was tested using nitrite reduction. The reduction current density (j) was normalized to the surface area of the nano-Fe/GC electrodes calibrated using a bulk Fe electrode, and used directly to compare the catalytic activities of different samples.

4. Two series of Fe NCs enclosed by different crystalline facets were synthesized by means of the programed potential-step route. We demonstrated that the shape of the Fe NCs can be finely tuned systematically by varying the electrochemical conditions, i.e., the growth potential and the concentration of $FeSO_4$ in solution. For example, with the increase of deposition overpotential, the Fe NCs were tuned from rhombic dodecahedra or tetragonal bipyramids bounded by {110} facets to a series of 18-facets polyhedra enclosed by different combinations of {110} and {100} facets, and finally to cubes of {100} facets. This result is in agreement with the two-dimensional nuclei theory, which indicates that the rate of formation of two-dimensional nuclei of the type {hkl} is proportional to $\exp(-W_{hkl}/k_BT)$ (where W_{hkl} is the work of formation of the {hkl} nuclei, k_B is Boltzman's constant, and T is the absolute temperature).

5. With the synthesized Fe NCs, the surface-structure functionality of the Fe NCs toward electrocatalytic reduction of nitrite was investigated. The result demonstrated clearly indicates that the electrocatalytic activity of the cubic Fe NCs with an opensurface {100} structure is much higher than that of the RD and TB Fe NCs enclosed with closest-packed {110} facets. The relationship between the surface structure of Fe NCs and their electrocatalytic activity toward nitrite reduction was analyzed by plotting the j value against the ratio of active surface atoms on an Fe NC (i.e., $R = N_{active}/N_{total}$). The result illustrated clearly that j increases with R, demonstrating that the electrocatalytic activity of the Fe NCs is enhanced by increasing the fraction of {100} facets on the Fe NC surface. This structural dependence of Fe NC electrocatalytic activity was also confirmed by the steady catalytic activity, which was measured from the time-dependent current density of nitrite reduction at a fixed potential over a long reaction time.

6. Fe octapods、dendritic and parallel intergrouth nanocrystals supported on glassy carbon were synthesized by means of the programed potential-step route. The surface

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