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Fe_2O_3、ZnO 纳米晶的表/界面结构控制及其相关性质的研究

Controlled Synthesis of Surface/Interfacial Structure of Fe_2O_3 and ZnO Nanocrystals and Related Properties

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Controlled Synthesis of Surface/Interfacial Structure of Fe_2O_3 and ZnO Nanocrystals and Related Properties

A Thesis Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Degree of Master of Science

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摘要

纳米材料因其独特的物理化学性质和在催化、气敏、光电器件等多方面的广阔应用前景引起了人们浓厚的研究兴趣，如何进一步提高其催化活性和利用效率一直是相关领域的重大科学问题和关键技术问题。表面是各类材料关键的组成部分，众多化学和物理过程都发生在表面上，表面结构的不同直接决定了材料的物理和化学性质的不同。因此，如何控制纳米材料的形貌和表面结构以调控材料相应的物理化学性质成为目前的一个研究热点。目前为止，合成出的纳米材料大多是以低能面裸露，而高能面裸露的纳米材料合成的较少。究其原因主要是晶体在生长的过程中，为了保持其表面能最小，具有高晶面能的晶面一般生长速度很快，随着晶体生长的进行将导致该晶面逐渐减小并消失，因此往往最终产物是以低能面裸露。但如果我们在晶体生长过程中，利用现有的知识体系，合理利用表面吸附剂、纳米晶自身的晶面特性以及其自主装等规律，在合适的实验条件下可以成功控制合成出具有高能面裸露的纳米材料。本课题组在金属氧化物半导体纳米晶如 TiO_2, SnO_2, ZnO 等的形貌和晶面控制方面做了很多有益的尝试，并得到有价值的科研成果。

另一方面，纳米异质结构由于其中组分存在的相互协同效应，使纳米异质结构材料的催化、气敏、光催化及光电效应等性能得到增强，在多种不同应用领域都得到了广泛的研究。然而，目前关于构建纳米异质结构的相关报导多数只是简单将一种物质负载或生长于另一种物质表面，而作为被负载的物质往往没有一个明确的形貌及裸露晶面，因此人们很少将材料的形貌、裸露晶面与异质结构所存在的界面相联系起来。所以，纳米晶不同晶面在异质结构的协同效应中的具体作用一直不明确。基于晶体不同晶面对其材料的化学性质的显著影响，我们有理由相信，纳米异质结构中，异质界面所处的具体晶面同样将明显影响整个纳米异质材料的性质。从材料特定裸露晶面的角度出发，对纳米异质结构的性能进行研究势必将成为今后的一个研究焦点。

本论文以 Fe_2O_3 和 ZnO 为主要研究对象，从控制表面结构出发，研究并探讨了它们的表面结构与其多种性质的关系。具体而言，主要分为四章，其内容

概括如下：

第一章：简要地对纳米晶表面结构与性质的联系、纳米晶的生长原理、调控形貌的方法以及金属氧化物纳米异质结构的性质研究及其应用进行了回顾和总结，并阐明了我们的研究意义和主要内容。

第二章：通过合理控制 Fe_2O_3 合成体系中的过饱和度，合成了具有{113}、{012}和{001}/{012}晶面裸露的三种不同形貌的 α-Fe_2O_3 纳米颗粒，并通过调控反应条件研究了体系过饱和度与产物形貌演变之间的关系。我们发现高的过饱和度更利于{113}这类具有较高晶面能的晶面生长；而低过饱和度更利于{113}，{001}这类具有较低晶面能，热力学更稳定的晶面生长。同时通过一系列 CO 催化氧化测试和气敏测试，我们发现不同 Fe_2O_3 晶面的 CO 催化氧化性能和气敏响应性与晶体表面化学吸附 CO 和氧的能力密切相关。

第三章：我们将先前合成出的三种形貌的 α-Fe_2O_3 纳米颗粒进行 Pt 光还原负载，通过对 Pt 负载后的样品以及第一次 CO 催化氧化测试后的样品进行了表征，我们发现利用光还原方法负载 Pt 所得 Fe_2O_3 样品表面的 Pt 主要是以 PtO_2 与 $Pt(OH)_2$ 的形式存在的，同时发现 Fe_2O_3 不同晶面能显著影响 PtO_2 与 $Pt(OH)_2$ 的含量，即能控制样品表面 Pt 的存在方式。此外，通过对 Pt 负载样品的 CO 催化氧化性能和催化稳定性测试我们发现，样品的 CO 催化氧化性能、催化稳定性以及表面化学吸附 CO 性能由 PtO_2 与单质 Pt 共同决定，其中 PtO_2 被证明具有更重要的影响。在气敏相应性测试中，我们发现 Pt 负载的{012}晶面的气敏响应性比未负载前有明显的提升。

第四章：通过热分解的方法成功合成了由(001)、$(00\bar{1})$和{101}三种极性面围成的 ZnO 六角锥/六棱台纳米晶，并通过紫外光下贵金属(Ag, Au)/MnO_2 的选择性负载研究了不同晶面对于光生电子/空穴迁移方向的影响。我们发现 ZnO 在紫外光激发下，光生电子/空穴分离后定向迁移至不同裸露晶面，导致不同裸露晶面还原/氧化能力的不同。其中光生空穴倾向于流向 $O^{2-}(00\bar{1})$面，将 Mn^{2+}氧化为 MnO_2；而光生电子倾向于流向 $Zn^{2+}(001)$面，导致贵金属(Ag, Au)倾向于在(001)面处负载。

关键词：金属氧化物，过饱和度，催化，气敏，纳米异质结构

Abstract

Nanoscale materials have attracted much attention due to their unique physical and chemical properties as well as their potential applications in catalysts, gas sensors, and optoelectronic nanodevices and so on. One critical scientific and technological issue of nanoscale materials is to further improve their corresponding activity as well as utilization efficiency. Surface is a special and important component of solid state materials. Since many chemical and physical processes take place on the surface of materials, the surface structure determines many surface related physical and chemical properties of the materials. Therefore, controllable synthesis of nanomaterials with specific crystal structures and various morphologies with different surface structure becomes a hot research topic nowadays. According to our knowledge, however, most of naturally and artificially grown nanocrystals are exposed with low energy facets, as high-energy surfaces usually diminish quickly for minimization of surface energy during a crystal growth process. Yet we believe that with our knowledge of crystal growth, we can create some proper crystal growth environments where nanocrystals exposed with high energy facets could be fabricated.

On the other hand, nanoscale heterostructured materials have been extensively studied due to the synergistic effects existed among the components of the heterostructured materials, which can significantly enhance the performances of materials in various fields such as catalysis, gas sensing, solar cells, etc. However, due to the difficulty of control synthesis of nanocrystals with specific surface, it is usually hard to study the heterostructures on specific crystal surfaces. According to our efforts on the control of surface structure of nanocrystals, we firmly believe that controllable synthesis of nanoscale heterostructure on specific surface of nanocrystals also plays a critical role in tuning the properties of the materials.

In this thesis, we respectively synthesized Fe_2O_3 and ZnO nanocrystals with specific surface structures and constructed noble metals/metal oxides nanoscale heterostructure on various crystal facets, and investigated their surface related properties. The thesis is composed by 4 chapters.

Chapter 1. Briefly review on the crystal surface structure and corresponding properties, crystal growth mechanism and properties/application of nanoscale heterostructure materials, as well as clarify my research significance and main contents.

Chaper 2. α-Fe_2O_3 nanocrystals exposed with {113}, {012} and {001}/{012} were successfully fabricated respectively by controlling supersaturation of growth species in the reaction. The effect of supersaturation on shape evolution of α-Fe_2O_3 nanocrystals was studied, which showed that the facets with high surface energy, such as {113}, tended to be formed in the reaction solution of high supersaturation, while the relatively more stable facets, such as {012} or {001}, were favored in the reaction solution of lower supersaturation. In addition, the differences of the catalytic activity in CO oxidation and sensing performances of these specific faceted nanocrystals were ascribed to the deferences of the adsorption capability to CO and oxygen species on different crystal facets.

Chapter 3. Pt was loaded on the previously fabricated α-Fe_2O_3 nanocrystals. From the characterization of Pt loaded samples, it was found that Pt mainly existed as the forms of PtO_2 and $Pt(OH)_2$, respectively, which also varied according to different crystal facets. Moreover, the catalytic activity of Pt loaded samples in CO oxidation was co-determined by Pt as well as PtO_2, where the latter one was proven to be more important. Gas sensing performances of these samples are all enhanced with existence of Pt, especially on the {012} facet.

Chapter 4. ZnO pyramid nanocrystals with (001), $(00\bar{1})$ and {101} polar crystal facets has been successfully synthesized, and the relationship between surface structures and migrations of photon-generated carriers has been studied by selective load of (Ag, Au)/MnO_2. It was discovered that, under ultraviolet light, holes tended to migrate towards $(00\bar{1})$ facet exposed with O^{2-}, turning $(00\bar{1})$ into an oxidizing facet, which led to the formation of MnO_2; on the other hand, electrons tend to migrate towards (001) facet exposed with Zn^{2+}, making (001) a reducing facet where noble metals (Ag, Au) were loaded.

Keywords: Metallic Oxide; Supersaturation; Catalysis; Gas sensor; Nanoscale Heterostructure.