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纳米材料的合成和纳米器件的制备: 从贵金属异质纳米结构到摩擦电纳米发电机

Synthesis of Nanomaterials and Fabrication of Nanodevices: from Noble Metal Heterogeneous Nanostructure to Triboelectric Nanogenerator

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**Synthesis of Nanomaterials and Fabrication of Nanodevices:
from Noble Metal Heterogeneous Nanostructure to Triboelectric
Nanogenerator**

A Dissertation Submitted for the Degree of Doctor of Philosophy

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摘 要

新材料和新能源的开发和利用对人类社会可持续发展具有重要意义,研发和探索新功能材料和可再生能源是当前面临的最迫切挑战之一。纳米科技是当今世界高新技术发展的支柱之一,也是新能源和新材料研发依赖的重要途径和方式。纳米材料和器件是纳米科技的核心和基础,纳米技术从基础到应用的一般途径是从纳米材料的合成到纳米器件的制备,再到更高一级的纳米系统的组装及应用。

本论文分为上下两篇,分别针对纳米材料的合成和纳米器件的制备和应用进行研究和论述。上篇是关于异质纳米结构的合成与表征,以及生长机理的系统性研究。下篇介绍了一种基于新原理开发的纳米发电机,可以从周围环境中有效地收集能量然后转化为电能用于驱动小型电子产品和器件。主要的研究内容和成果如下:

上篇一,我们发展了一种简单有效的方法用于水相体系中合成均一的核-壳异质金属纳米粒子,以 Au 纳米八面体作晶种合成了高质量的 Au@Pd、Au@Ag 纳米立方体和 Au@Pt 多晶纳米球。基于对两种不同生长模式的系统研究,我们首次提出了异质金属外延生长的一般规则,核-壳金属的原子半径、金属键能以及电负性各自对应的匹配关系在决定层状外延生长模式中起关键作用。对生长模式的系统性研究和总结的规则将有助于设计和合成其它复杂形式的异质纳米材料,如多层结构和金属-半导体杂化结构。

上篇二,为了研究清楚核-壳型异质金属纳米结构如何释放晶格不匹配产生的应力,我们对包覆有不同 Pd 壳层厚度的 Au@Pd 纳米晶体的表面和界面结构进行了详细的表征和分析。结果证实当 Au 核表面只包覆有单层或亚单层 Pd 原子时,晶格失配产生的应力通过肖克利局部位错伴随堆垛层错的形式释放;当 Au 表面包覆有多层 Pd 原子之后,晶格失配的应力释放则是依靠 Au 原子扩散到 Pd 壳层中形成长程有序的 $L1_1$ Au-Pd 合金结构来完成。这项研究揭示了 Au-Pd 体系存在较大的晶格失配度的情况下仍然采用层状外延生长模式的根本原因。

上篇三,我们利用纳米晶体晶面间结构的差异,选择性地生长单晶 ZnO 纳米棒在 Ag 立方八面体的 {111} 晶面而非 {100} 晶面上,合成了 Ag-ZnO 异质纳米结构。通过对异质结构的详细表征初步确认生长层和基底之间的结构匹配性在这

种新的晶面选择性外延生长的模式中起决定性作用。为了研究 Ag 和 ZnO 之间界面处的电学性质，我们以多步生长法合成的微米级 Ag 立方体和 Ag 线作晶种，制备出显微镜下容易操控的单个异质结构器件。测试结果证实了异质结构中 Ag 和 ZnO 之间界面处是典型的肖特基接触。这类异质结构在功能器件、生物传感器和催化等领域具有潜在的应用价值。

下篇一，基于聚合物材料摩擦起电和静电感应相结合的原理，我们利用一种全新的、简单而有效的方法可以将机械能转换成电能用于驱动小型电子设备。摩擦电发电机（TEG）由两种镀有金属电极的聚合物薄膜组装而成，在外力作用下器件中的聚合物膜产生形变和相互摩擦，形成电荷分离和电势差，并驱动电子在外电路中流动。单个器件的输出电压达到 3.3V，峰值功率密度 10.4 mW/cm^3 。这项研究为功能性和自驱动的有机纳米器件的设计和应用开辟了一条新的途径。

下篇二，透明、柔性和高效率的电源输出装置将是未来有机电子和光电子器件的重要组成部分。在第一代摩擦电发电机的基础上，我们采用透明高聚物材料制备了一种新的高性能输出的柔性透明纳米发电机。借助光刻、蚀刻和模板工艺在聚合物表面制备了均一规则的微型阵列结构，将纳米发电机的输出效率提高了四倍。此外，所制备的纳米发电机可作为一种自驱动的主动式压力传感器，用于感测微弱的压力和振动，如水滴或羽毛落下时产生的轻微碰触。

下篇三，摩擦电发电机结构简单、新颖，输出性能高，在工业生产和实际应用中与目前其它类型的微型发电机相比具有明显的优势。摩擦电发电机在自驱动系统中展现出很好的应用前景，它可以通过人体运动、海浪、机械振动等多种方式和途径收集能量，进而转化为电能应用于个人电子产品、环境监测、医疗科学甚至是宏观电源装置。

关键词：异质纳米结构，外延生长，晶格失配，纳米发电机，摩擦电效应，压力传感器

Abstract

Research on functional materials and renewable energy sources is of great significance and one of the most urgent challenges to the sustainable development of human civilization. Nanotechnology has become one of the high-tech pillars in today's world, but also provides the potential ways to address some of the critical challenges faced by new materials and new energy. As the key and foundation of nanotechnology, the synthesis of nanomaterials and fabrication of nanodevices with the higher-level assembly of nanosystem in turn constitute a general approach from the basic research to application. This doctoral thesis is divided into two parts. Part I mainly focused on synthesizing and characterizing multifunctional heterogeneous nanostructures and systematically investigating the growth mechanism. Part II aims to design and fabricate a novel nanogenerator based on the new principle to efficiently harvest energy from the environment for self-powering small electronics and devices. The main research works are listed as follows:

I-1 We developed a simple and effective route to synthesize uniform heterogeneous single-crystal Au@Pd and Au@Ag nanocubes from octahedral Au nanocrystals seeds in aqueous solution. Based on the systematic study on the heterogeneous growth mechanism, we have preliminarily proposed a general rule that the atomic radius, bond dissociation energy, and electronegativity of the core and shell metals play key roles in determining the conformal epitaxial layered growth mode. This rule would be help for designing and fabricating more complex nanostructures, such as multiple-shell nanostructures and metal-semiconductor nanocomposites.

I-2 To study the mismatch-release mechanism in core-shell nanoparticles, we systematically characterized and analyzed the interfacial structure of Au@Pd nanoparticles with controlled Pd-shell thickness. For Au core coated with single atomic layer of Pd, the mismatch strain is released by Shockley partial dislocations (SPDs) accompanied by the formation of stacking faults. For nanoparticles coated with more Pd (>2 nm), the diffusion of Au atoms into the Pd shell layers that form a stable and long-range ordered $L1_1$ Au-Pd alloy phase. This study reveals the fundamental reason for the conformal epitaxial growth of Au@Pd nanoparticles with a large lattice mismatch.

I-3 We demonstrate a new approach for synthesizing Ag–ZnO heterogeneous nanostructures in which single-crystalline ZnO nanorods were selectively grown on {111} rather than {100} facets of Ag truncated nanocubes. We proposed a mechanism indicating that the structure match plays a critically important role in this new growth type. To study the electrical properties of the interface between Ag and ZnO, we prepared single heterostructured device using microscale Ag structures as seeds and identified the Schottky contact at the interface. These heterogeneous structures are of special interest and have potential applications in electrical contacts, functional devices, biological sensors, and catalysis.

II-1 We have demonstrated a new, simple and effective approach of using the triboelectric effect and electrostatic induction of polymeric materials to convert mechanical energy into electric power for driving small electronics. The triboelectric generator (TEG) is fabricated by stacking two polymer sheets with metal films deposited on the surfaces. This study opens up a new way towards the design and application of functional and self-powered organic nanodevices.

II-2 On the basis of the first generation of TEG, we demonstrate a new high-output, flexible and transparent nanogenerator by using transparent polymer materials. We have fabricated regular and uniform polymer patterned arrays to improve the output efficiency up to four times as high as the previous TEG. Furthermore, the as-prepared nanogenerator can be applied as a self-powered active pressure sensor for sensing the subtle pressure and vibration, such as the falling of a water droplet and feather.

II-3 TEG exhibits great advantages in industrial production and practical applications and shows a potential of harvesting energy from human activities, ocean waves, mechanical vibration and more, with great applications in self-powered systems for personal electronics, environmental monitoring, medical science and even possibly large-scale power.

Keywords: Heterogeneous nanostructures; Epitaxial growth; Lattice mismatch; Nanogenerator; Triboelectric effect; Pressure sensor

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